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FLUIDITY AND VAPOR PRESSURE

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[THIRTEENTH COMMUNICATION BEARING ON THIS SUBJECT]

In an earlier article it was pointed out that there is an intimate relation between fluidity and vapor pressure. The vapor pressures of the saturated aliphatic hydrocarbons, when plotted against the fluidities corresponding to the same temperatures, give a single curve for this whole class of substances with fair precision. In other words, the known relation that the fluidity of all of these substances is nearly identical at the particular vapor pressure of 760 mm. is only a particular case of the more general relation that *at any given vapor pressure, the saturated aliphatic hydrocarbons have the same fluidity*. Nor is this relation confined to a single class, for it has been shown[2] to be at least as equally true of the ethers. In this simple form, it appeared that the relation could not be made perfectly general, for the fluidities of other classes are by no means identical at the boiling point. But that the underlying relation is operative is shown by the fact that the fluidities, at the boiling point, of all classes of unassociated compounds are related to each other in a linear manner.[3] The approxi-

[1] THIS JOURNAL, **43**, 295 (1910).
[2] *Loc. cit.*
[3] Z. physik. Chem., **66**, 1 (1909).

mate identity of the fluidities of the hydrocarbons and ethers s only an accident perhaps, the slope of the boiling point-fluidity curve being very small. Therefore, it is important to formulate the underlying relation and to prove that it is perfectly general, if indeed that is possible.

The fluidity-vapor pressure curves of all unassociated compounds are similar but not coincident. Now the fluidity of the aliphatic hydrocarbons at their boiling points is around 500 cm. $g.^{-1}$ sec. Taking the round number 500 as the standard, all other fluidities may be reduced to those of a substance which has a fluidity of 500 at the boiling point; the general properties of the curve remain the same as before. Thus heptane has a fluidity at the boiling point (98°.4 C.) of 503.9. At 90° heptane has a fluidity of 468.3 absolute units and a vapor pressure of 588.8 mm. Reducing this fluidity to standard, we have $468.3 \times 500 \div 503.9 = 464.7$. An extensive study of the fluidities of substances at a given temperature has led to the belief that this method of reduction is legitimate, certainly in a general way. The reasons for this belief need not be given here, since it will be seen at once that this method of reduction merely shifts the vapor pressure-fluidity curves so that at the ordinary boiling temperatures they will be coincident. By this means the comparison of the curves at other temperatures is facilitated. Plotting the reduced fluidities of heptane against the observed vapor pressures, a curve is obtained which will here be arbitrarily regarded as the standard fluidity-vapor pressure curve. The reduced fluidity-vapor pressure curves of other substances will be studied in relation to this arbitrary standard.

The values of the vapor pressure read from this curve for every five units of fluidity, except for vapor pressures below 100 mm., are as follows:

Table I.—Fluidities and Vapor Pressures Corresponding to the Standard Fluidity-Vapor Pressure Curve

Fluidity reduced	Vapor pressure in mm.	Fluidity reduced	Vapor pressure in mm.	Fluidity reduced	Vapor pressure in mm.
100	0.5	310	111.1	420	396.7
110	0.7	315	119.0	425	415.7
120	1.0	320	127.8	430	434.9
130	1.7	325	136.5	435	455.5
140	2.2	330	146.1	440	476.1
150	3.0	335	155.4	445	497.3
160	4.3	340	165.2	450	520.0
170	6.1	345	175.5	455	542.5
180	8.2	350	186.2	460	566.8
190	11.0	355	197.6	465	589.5
200	14.2	360	210.4	470	614.7
210	17.7	365	223.2	475	635.9
220	22.3	370	236.6	480	660.1
230	27.7	375	251.0	485	683.7
240	34.1	380	266.0	490	711.7
250	41.2	385	281.1	495	736.3
260	49.3	390	296.2	500	760.0
270	58.8	395	311.4	505	783.8
280	69.1	400	328.3	510	810.0
290	81.8	405	344.7	515	838.8
300	95.9	410	360.7	520	869.5
305	103.2	415	378.4	525	902.0

The use of the above table is obvious. Of the substances whose fluidities are known, the vapor pressures of only a part are known over a considerable range. By studying the agreement between the observed values and the values of the vapor pressure as calculated from the standard curve, an idea may be gained as to the value of this method for calculating vapor pressures in general. This comparison is made in the following tables. The fluidities are those already published and are based on the elaborate measurements of Thorpe and Rodger.[1] They have been reduced as described above. The fluidities at the boiling points, required for the reduction, were read from the fluidity curves of the different substances by Miss Harrison several years ago, in the course of an investigation

[1] Phil. Trans., **185, A,** 397 (1894).

with the author of this paper. The vapor pressures were in part measured by the author, the remainder being taken from the *Tabellen* of Landolt, Börnstein and Meyerhoffer. The reduced fluidities are given under φ_r, vapor pressures in millimeters under p. Observed fluidities are designated by φ:

Table II.—The Vapor Pressures of Hydrocarbons Calculated from their Fluidities Reduced to 500 C. G. S. Units at the Boiling Point

	Pentane				Hexane			
Temp.	φ_r	p obs.	p calc.	Per cent. diff.	φ_r	p obs.	p calc.	Per cent. diff.
0	354.9	183.25	197.1	8	256.6	45.4	46.4	2
10	392.9	281.8	305.0	8	286.6	75.0	77.2	3
20	432.6	420.2	445.0	6	317.7	120.0	123.3	3
30	474.2	610.9	633.0	4	350.6	185.4	187.2	1
40	(513.6)	873.0	829.3	—12	385.2	276.7	281.6	2
50					421.9	400.9	403.8	1
60					460.3	566.2	569.3	0
70					502.8	787.0	770.1	—2
	φ = 497.9 at b. pt., 36°.3				φ = 491.7 at b. pt., 69°.4			

	Octane			
Temp.	φ_r	p obs.	p calc.	Per cent. diff.
0	140.8	2.9	2.3	—20
10	161.9	5.6	4.8	—14
20	184.2	10.4	8.9	—14
30	207.2	18.4	16.8	— 9
40	231.5	30.8	28.6	— 7
50	257.1	49.4	46.9	— 5
60	283.8	77.6	73.7	— 5
70	311.7	117.9	113.7	— 4
80	341.2	174.8	167.5	— 4
90	372.8	253.5	244.1	— 4
100	405.4	353.6	345.5	— 2
110	439.5	481.9	473.5	— 2
120	477.7	646.4	648.2	0
130	518.3	859.0	859.3	0
	φ = 504.7 at b. pt., 125°.3			

Table III.—The Vapor Pressures of Ethers Calculated from their Fluidities Reduced to 500 C. G. S. Units at the Boiling Point

Temp.	φ_r	p obs.	p calc.	Per cent. diff.
Diethyl				
0	359.6	184.9	209.0	8
10	396.8	291.8	316.8	9
20	427.1	442.4	424.8	—4
30	478.9	647.9	653.4	1
40	524.1	921.2	897.0	—2
φ = 487.9 at b. pt., 34°.8				
Methylpropyl				
	343.9	156.0	173.0	11
	381.5	242.6	270.5	12
	419.8	373.4	395.5	6
	461.8	552.5	577.0	5
	503.7	784.0	775.8	—1
	φ = 473.2 at b. pt., 39°.1			
Ethylpropyl				
0	262.7	52.1	51.9	0
10	294.3	88.5	87.8	—1
20	328.1	142.6	142.5	0
30	363.5	219.5	219.5	0
40	400.8	327.9	330.7	1
50	439.8	476.7	475.1	0
60	481.9	670.2	668.2	0
70				
80				
90				
φ = 479.9 at b. pt., 63°.4				
Dipropyl				
	196.4	22.4	13.0	—43
	223.0	31.8	23.9	—26
	252.5	51.0	43.1	—16
	282.8	82.0	72.7	—11
	314.3	125.6	118.2	— 5
	348.0	189.6	181.9	— 4
	382.7	281.8	273.9	— 3
	419.8	404.2	395.5	— 2
	458.8	563.6	561.1	0
	501.1	776.0	762.2	— 2
	φ = 471.5 at b. pt., 89°.8			

Table IV.—The Vapor Pressures of Esters Calculated from their Fluidities Reduced to 500 C. G. S. Units at the Boiling Point

Temp.	φ_r	p obs.	p calc.	Per cent. diff.
Methyl formate				
0	361.9	195.0	215.0	10
10	404.0	309.4	341.5	10
20	447.2	476.4	509.2	7
30	490.5	707.9	711.0	0
40				
50				
φ = 321.9 at b. pt., 31°.8				
Ethyl formate				
	286.7	72.4	77.1	7
	322.5	120.3	132.1	2
	368.2	192.5	231.2	20
	399.9	297.5	328.1	10
	441.0	446.7	481.0	7
	482.5	649.4	672.0	3
	φ = 345.7 at b. pt., 54°.2			

Table IV—(Continued)

	Propyl formate				Methyl acetate			
0	208.8	21.4	17.2	—18	277.6	62.1	66.6	7
10	238.2	37.8	32.9	—15	312.0	104.8	114.1	9
20	269.8	63.9	58.7	— 8	348.2	169.8	182.3	7
30	303.3	104.1	100.7	— 3	386.1	265.8	284.8	7
40	338.4	163.6	161.9	— 1	425.4	400.4	417.3	4
50	374.9	249.4	250.1	0	467.1	588.2	599.0	2
60	414.2	364.9	375.7	3				
70	454.9	523.9	542.1	3				
80	497.2	734.5	742.8	1				
	$\varphi = 359.0$ at b. pt., 80°.9				$\varphi = 376.8$ at b. pt., 57°.1			

	Ethyl acetate				Propyl acetate			
0	218.7	24.3	21.8	—11	161.2	7.4	4.7	—36
10	249.3	42.7	40.7	— 5	186.7	13.9	10.0	—28
20	280.8	72.8	70.1	— 4	213.8	25.1	19.4	—23
30	315.8	118.7	120.4	1	243.2	42.7	36.3	—15
40	350.9	186.2	188.0	1	273.4	70.8	62.0	—12
50	380.2	282.2	266.7	— 5	304.7	112.2	102.6	— 8
60	426.6	415.4	422.5	2	338.1	171.8	161.7	— 6
70	467.6	596.3	601.4	1	372.3	257.3	243.1	— 5
80					409.7	372.8	359.3	— 4
90					450.0	524.8	520.0	— 1
100					490.9	723.6	712.2	— 1
	$\varphi = 395.6$ at b. pt., 77°.2				$\varphi = 400.5$ at b. pt., 101°.5			

	Methyl propionate				Ethyl propionate			
0	218.8	21.9	21.7	— 1	175.0	8.3	7.1	—14
10	248.3	38.8	40.0	3	200.3	15.6	14.3	— 8
20	279.8	66.2	68.8	4	227.7	27.8	26.3	— 5
30	312.0	107.8	114.2	6	256.8	47.8	46.7	— 3
40	346.2	169.3	178.0	5	286.8	77.9	77.6	0
50	381.3	256.7	269.8	5	318.6	123.0	125.1	2
60	418.7	380.3	391.2	3	351.5	188.0	189.5	1
70	458.8	548.0	560.0	2	386.8	279.9	283.2	2
80					423.8	403.6	411.0	2
90					462.6	569.5	580.9	2
	$\varphi = 393.0$ at b. pt., 79°.7				$\varphi = 412.8$ at b. pt., 99°.1			

Table IV—(Continued)

	Methyl butyrate				Methyl isobutyrate			
0	164.9	7.3	5.1	—30	187.3	12.2	10.2	—17
10	190.4	13.8	11.3	—18	214.7	22.4	19.8	—12
20	217.5	24.6	21.2	—14	243.3	38.9	36.5	— 6
30	246.1	41.9	38.3	— 9	273.0	65.4	61.7	— 6
40	276.4	69.2	65.3	— 6	304.7	104.7	102.9	— 2
50	307.1	109.6	106.8	— 3	338.3	162.0	162.0	0
60	340.1	167.5	165.7	— 1	372.8	243.8	244.4	0
70	374.6	250.3	249.2	0	409.6	355.2	359.3	1
80	410.9	361.4	363.2	0	449.2	505.0	517.6	2
90	449.5	507.0	517.2	2	490.9	707.0	716.0	1
100	488.5	700.7	704.3	1				
	φ = 400.0 at b. pt., 102°.7				φ = 397.3 at b. pt., 92°.3			

When we consider that one millimeter of error in the vapor pressure of octane at 0° corresponds to a percentage error of over 30, we must regard the agreement here displayed between the different classes as remarkable. The agreement is quite as good between the classes as between the members of a single class of compounds. The agreement is not perfectly satisfactory, but this may be due to a variety of causes. The compounds may be associated; the method of reducing the data to comparable conditions may not be entirely legitimate; the substances used in measuring the fluidity and vapor pressure may not have been equally pure. The values of vapor pressure given by different observers differ among themselves by several per cent. So there are numerous chances for the multiplication of error. Nevertheless, for vapor pressures of over ten centimeters the calculated values differ from the observed only by a little over 3 per cent.

The fluidities of some substances are known over a considerable range of temperature, but the vapor pressures are in some cases unknown, and it has also been shown in a previous communication[1] that the fluidity of unknown substances may be calculated. From this data and Table I, it becomes possible to calculate the unknown vapor pressures, it being only necessary to know the boiling point of the compound so long as the compound is unassociated. Conversely, if we know the vapor pressures of a substance and the fluidity at

[1] Z. physik. Chem., **66**, 1 (1909).

the boiling point, it becomes possible to construct the fluidity curve. This may become of practical use, for there have been few attempts to measure the fluidity of a liquid from the ordinary boiling point up to the critical temperature, yet the vapor pressures over this range have often been the subject of investigation. The following is a single illustration of the process of calculating fluidities from vapor pressures: Suppose that the fluidity of ethylpropyl ether at 20° is desired, it being known that the fluidity of this substance at the ordinary boiling point is 479.9 and that its vapor pressure at 20° is 142.6 mm. The corresponding fluidity read from the curve or interpolated from Table I is 328.0, but as these fluidities are reduced fluidities, they must be corrected; thus $328.0 \times 479.9/500 = 314.8$, which is practically identical with the observed value of 314.9 mm.

A priori, one would hardly expect to find any relation at all existing between the fluidity of a liquid and the vapor pressure of the vapor above it. Yet it is proved that there exists a simple relation between them. This is doubtless the result of both of these properties being similarly dependent upon another property of the liquid, which is probably the molecular volume.

The problem of association is at once so important and yet so baffling that it seems well to make a study of the fluidity-vapor pressure curves of a few associated compounds. The calculated values of vapor pressure are extremely divergent from the values obtained by observation, as is shown in the following specimen tables.

The percentage differences between the observed and the calculated values of vapor pressure are greatest for isobutyl alcohol and formic acid. In Fig. I the fluidities (not reduced) of several substances have been plotted against their vapor pressures. We note at once that isobutyl alcohol and formic acid are the two substances having the smallest fluidities at any given vapor pressure, so that the factor in their reduction was larger than for any other substances. Why the vapor pressures of formic acid at a given fluidity are abnormally large as compared with other acids is an interesting

Table V.—The Vapor Pressures of Some Associated Compounds Calculated from their Fluidities Reduced to 500 C. G. S. Units at the Boiling Point

Water

Temp.	φ_r	p obs.	p calc.	Per cent. diff.
30	177.4	31.6	7.8	—76
40	216.5	55.0	20.4	—64
50	258.1	92.2	47.9	—48
60	301.8	149.2	98.2	—34
70	348.5	233.8	182.7	—22
80	396.9	355.5	317.3	—11
90	448.2	526.0	512.8	— 2
100	500.0	760.0	760.0	0

φ = 353.4 at b. pt., 100°

Methyl alcohol

φ_r	p obs.	p calc.	Per cent. diff.
319.1	158.9	126.2	—20
364.4	259.4	222.0	—15
415.0	409.4	378.2	— 8
469.9	624.3	614.8	— 2

φ = 304.3 at b. pt., 65°.0

Ethyl alcohol

30	227.9	78.1	26.4	—66
40	272.4	133.4	61.0	—54
50	324.3	129.8	135.2	—39
60	382.3	350.2	273.0	—25
70	447.6	540.9	510.0	— 6

φ = 226.7 at b. pt., 78°.4

Butyl alcohol

70	219.7	102	22.1	—78
80	267.3	165	56.3	—66
90	321.0	257	129.7	—50
100	381.0	388	369.5	— 5
110	447.5	575	510.5	—11

φ = 245.8 at b. pt., 117°.3

Isobutyl alcohol

30	79.8	17.0	0.3	—99
40	107.5	31.6	0.5	—99
50	141.8	56.2	2.3	—96
60	183.0	96.2	9.0	—91
70	233.4	158.6	30.0	—55
80	292.3	252.2	85.0	—66
90	359.1	388.4	208.2	—46
100	436.8	580.1	463.0	—27

φ = 220.0 at b. pt., 107°.8

Formic acid

30	183.4	52.1	9.2	—83
40	218.8	82.3	21.8	—74
50	258.0	126.4	47.8	—63
60	299.8	189.2	95.5	—50
70	344.3	276.0	174.0	—31
80	390.5	393.4	298.0	—29
90	439.0	548.4	473.0	—14
100	492.5	749.0	719.8	— 4

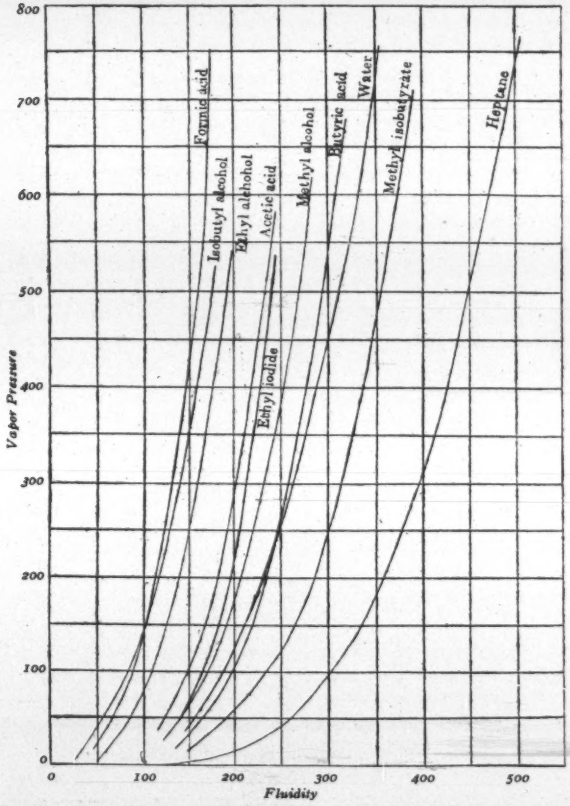
φ = 187.6 at b. pt., 101°.0

Acetic acid

Temp.	φ_r	p obs.	p calc.	Per cent. diff.
30	186.9	20.6	10.1	—50
40	214.9	34.8	20.0	—40
50	245.0	56.6	37.7	—34
60	276.3	88.9	65.3	—26
70	309.8	136.0	110.8	—11
80	345.7	202.3	177.0	—12
90	384.3	293.7	276.2	— 6
100	423.1	417.1	409.0	— 2
110	464.9	580.8	589.1	+ 1

φ = 258.2 at b. pt., 118°.1

question to whose answer we can suggest no clue. Isobutyl alcohol plays a similar role among alcohols. Whatever may



be the cause of this peculiarity, it is clear that the size of the factor used in reduction is not responsible for the difference

between the observed and calculated values of vapor pressure, for the percentage difference is by no means proportional to the size of the factor. This is shown in Table VI. Besides, there are some unassociated substances which show small differences between the observed and calculated values of the vapor pressure, and which, nevertheless, have quite small fluidities at the boiling point, e. g., ethyl iodide.

The percentage difference is far greater for the associated than for the unassociated compounds, but unfortunately the relation between the percentage difference and the amount of association does not amount to a direct proportionality. This is also shown in Table VI.

Table VI.—A Comparison between the Factor Used in Reducing the Fluidities, the Association and the Average Percentage Difference between the Observed and the Calculated Values of the Vapor Pressure of Some Associated Compounds

Substance	Factor	Association	Average percentage difference
Butyric acid	1.55	1.51	10
Methyl alcohol	1.64	1.84	11
Ethylene bromide	2.57	1.09	20
Benzene	1.59	1.17	20
Water	1.42	2.31	32
Ethyl alcohol	2.21	1.83	38
Formic acid	2.66	2.05	44
Isobutyl alcohol	2.27	1.66	72

The important thing seems to be that the slope $dp/d\varphi$ of the vapor pressure-fluidity curves of associated compounds is smaller than would be expected from a study of unassociated compounds. This is proved by the fact that the observed values of the vapor pressure of associated compounds, at low temperatures, are invariably much higher than the calculated values. The percentage difference in the case of isobutyl alcohol is much greater than in the case of formic acid, although the association and the factor used in reduction are both considerably smaller, and the curves cross each other; but as can be seen by inspection of the figure, the slope of the curve for isobutyl alcohol is considerably smaller than that for formic acid. The same is true of other pairs, some of which are to be ob-

served in the figure, viz., ethyl iodide and methyl alcohol, butyric acid and water. The effect of association upon fluidity seems to be known, hence the effect here pointed out would seem to be that of association upon vapor pressure. The vapor pressures of associated substances therefore appear to increase less rapidly than would be expected from our study of unassociated substances. Were we able to give quantitative expression to this effect we might be able to eliminate the differences between the observed and calculated values in the case of associated compounds. The relation which has here been pointed out would then be made perfectly general. At present this cannot be done.

CONCLUSIONS

It has been shown that the fluidity and vapor pressure of unassociated compounds are simply related to each other. If the fluidity of all unassociated compounds at their boiling points (760 mm. vapor pressure) be multiplied by such a factor that these compounds at the boiling point may have the same fluidity—arbitrarily chosen as 500——then any fluidity whatever, when multiplied by the factor for the given compound and plotted against the vapor pressure observed at the same temperature, will fall on a single curve for all of these substances.

If follows that the vapor pressure of liquids may be calculated provided that only their fluidities and ordinary boiling point are known. Seventeen substances have been here compared over a range of temperature, and for vapor pressures over 100 mm. it has been found that the average percentage difference between the observed and the calculated vapor pressures is a little over 3 per cent. The relation does not hold good for highly associated substances. This appears to be due to the vapor pressure of associated substances increasing more slowly than would be expected from a study of the fluidity-vapor pressure curves of unassociated compounds.

RICHMOND COLLEGE
RICHMOND, VA.
Oct. 29, 1911

[Contributions from the Chemical Laboratory of Harvard University]

CERTAIN DERIVATIVES OF TETRACHLORORTHOBENZOQUINONE[1]

By C. Loring Jackson and G. L. Kelley

In 1907, R. D. MacLaurin and one of us described a number of substances prepared from tetrachlororthobenzoquinone, several of which in the time at our disposal could not be studied thoroughly enough to determine their nature. In this paper we describe the continuation of the study of three of these.

By the action of benzyl alcohol on tetrachlororthoquinone MacLaurin and one of us[2] obtained a yellow substance crystallizing in square prisms and melting with decomposition (under certain conditions) at 215°, which gave analytical results not far from the percentages for the ether $C_6Cl_4O_2C_6Cl_2(OH)_2$, but as this melts at 290° and differs from the new substance in many other respects, it was impossible even to assign a formula to it. When we took up again the study of this body, we were struck with the facts that its melting point, 215°, agreed with that of the heptachlororthoquinopyrocatechin hemiether (214°) discovered in the meantime by P. W. Carleton and one of us,[3] and like that it was converted into the red ether, $C_6Cl_4O_2C_6Cl_2O_2$, by alcohol; but the chlorine determinations were 4 per cent. below those required by this formula. A possible explanation of this difference was suggested by the fact that the corresponding heptabrom hemiether[4] crystallizes with one and a half molecules of benzene and also in square prisms. Upon calculating the percentage of chlorine in $(C_6Cl_4(OH)OC_6Cl_2O_2)_2C_6H_6$ we found that it agreed with the results of the chlorine determinations, but the percentage of carbon in this formula was over 2.5 per cent. above that found; this might well be accounted for by supposing the specimen used for his combustion by Dr. Mac-

[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by George Leslie Kelley.

[2] This Journal, **38**, 165 (1907).

[3] *Ibid.*, **39**, 499 (1908).

[4] Jackson and Russe: *Ibid.*, **35**, 166 (1905).

Laurin had lost part of its benzene, but we have not thought it worth while to prove this by repeating the combustion of this substance, as the following experiments establish the presence of one-half molecule of benzene[1] in the compound. A specimen of the substance heated at 80° showed a loss corresponding to this amount of benzene, but the result cannot be considered conclusive, because the heptachlor body is easily decomposed by heat, so that something beside benzene may have escaped. That no hydrochloric acid was given off at this temperature was proved by a special experiment, and this was the most probable decomposition product, as it was formed in quantity[2] between 110° and 140°. A specimen of the substance from benzyl alcohol was crystallized three times from ligroin, which raised the percentage of chlorine to about 0.6 per cent. below that calculated for $C_6Cl_4(OH)OC_6Cl_3O_2$. Some of the heptachlor hemiether made in the usual way was purified by crystallization from benzene and ligroin instead of chloroform, when upon analysis it was found to contain the amount of chlorine corresponding to

$$(C_6Cl_4(OH)OC_6Cl_3O_2)_2C_6H_6.$$

The presence of benzene in the product from benzyl alcohol was shown by heating it with nitric acid, when nitrobenzene was recognized by its smell. The properties and reactions of the two substances agree also in the closest way, except for the difference in crystalline form, which would be expected from the presence of the benzene of crystallization. On boiling with water our substance was converted into the red ether, $C_6Cl_4O_2C_6Cl_2O_2$, and the loss corresponded to that of $2HCl + C_6H_6$ required by the theory.

So far as we could find, the only products of the reaction of benzyl alcohol on tetrachlororthoquinone beside the heptachlor-*o*-quinopyrocatechin hemiether are hydrochloric acid and benzaldehyde (recognized by its smell); it appears therefore that the benzyl alcohol acts by reducing some of the tetra-

[1] When crystallized from benzene instead of benzene and ligroin, crystals of a different shape were obtained, which were efflorescent, and may correspond to the bromine compound with one and a half molecules of benzene.

[2] THIS JOURNAL, **39**, 500 (1908).

chlorquinone to tetrachlorpyrocatechin, each molecule of which at once combines with another molecule of the quinone to form the hemiether. This behavior of the tetrachlorquinone is interesting because it is entirely different from that of the tetrabrom-*o*-quinone, which combines with benzyl alcohol to form the α compound, $(C_6Br_4O_2)_2C_7H_7OH$.[1] No indications of the formation of an α-chlor compound have been observed.

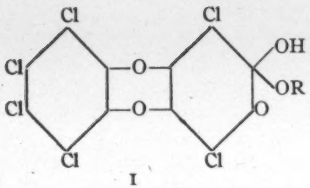
That the benzyl alcohol derivative was the heptachlor hemiether was confirmed by analyses of its acetyl compound[2] melting at 195°, the product of its reduction,

$$C_6Cl_4(OH)OC_6Cl_3(OH)_2,$$

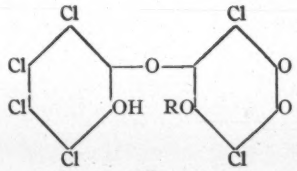
melting at 188°–190°, and the triacetyl compound of this last, melting at 144°.

The next substance studied by us was the compound formed by the action of ethyl alcohol on tetrachlor-*o*-quinone,[3] which crystallizes in orange-yellow hexagonal prisms melting at 210°. Molecular weight determinations of this substance had been made by the boiling-point method, but as it had been found subsequently that special precautions were necessary to obtain correct results by this method under the unfavorable conditions existing in our organic laboratory, we repeated them by the freezing-point method, and in this way found that the formula of this substance is $C_{12}Cl_6O_4C_2H_5OH$, which recalls that of the product melting at 198° obtained by the action of methyl alcohol on tetrachlor-*o*-quinone. In the previous work it was supposed that this substance was a hemiacetal (formula I), because it was formed by the action of the alcohol on the ether $C_6Cl_4O_2C_6Cl_2O_2$, but in taking up the study of the ethyl compound the second formula, that of the hemiether, seemed to us also worth consideration. The methods of preparation, of which several were discovered, furnished no conclusive evidence as to the constitution, but this was obtained by reduction with sulphurous dioxide, giving a product melting at 173°, and showing a percentage of chlorine

[1] Jackson and Porter: THIS JOURNAL, **31**, 100 (1904).
[2] *Ibid.*, **38**, 166 (1907).
[3] Jackson and MacLaurin: *Ibid.*, 159.



I



II

essentially the same as that obtained from the mother substance, as would be expected from the formula

$$C_6Cl_4(OH)O(C_2H_5O)C_6Cl_2(OH)_2.$$

Its nature was established by converting it into the acetyl derivative melting at 165°, which contained 3 acetyl groups and the ethyl. As such a compound cannot be obtained from a substance having Formula I, it follows Formula II is the correct one, and the substance is hexachlorethoxy-*o*-quinopyrocatechin hemiether.

We next tried similar experiments with the methyl compound melting at 198° and corresponding to the ethyl derivative in composition, but at first could not succeed in getting any reduction with agents which had reduced the ethyl compound, or, if the reaction worked at all, only the ether

$$C_6Cl_4O_2C_6Cl_2(OH)_2$$

was formed. These observations made us believe that the two compounds had a different constitution,[1] and this view received some support from the facts that the methyl derivative crystallized in needles instead of the rhombic plates of

[1] This view was published in a preliminary paper: Ber. d. chem. Ges., **42**, 1865 (1909).

the ethyl compound, and melted at a lower temperature (198°) than the latter (210°); it also gave a dimethyl derivative, whereas no such body has been obtained from our ethyl compound. A more careful study, however, at last led us to a method by which the reduction of the methyl derivative was accomplished; this consisted in treatment with sulphurous dioxide, alcohol and zinc dust, which gave a reduction product melting at 191°, and the triacetyl compound,

$$C_6Cl_4(OC_2H_2O)O(CH_3O)C_6Cl_2(OC_2H_3O)_2,$$

melting at 128°–129°, thus proving that Formula II belongs also to the methyl derivative in spite of the anomalous crystalline form, melting point and derivatives. This inference is confirmed by the observation that neither the methyl nor ethyl compound is decomposed by strong hydrochloric acid, whereas a hemiacetal (Formula I) should lose alcohol easily with this reagent.

Other reactions observed with these substances, which could not be used in determining their structure, are the formation of chloranilic acid with alkalies, the formation of the ether $C_6Cl_4O_2C_6Cl_2O_2$ with strong sulphuric acid or, to a certain extent, with acetyl chloride or acetic anhydride, of the reduced ether by zinc and acetic acid, and of a monoacetyl derivative. It is a curious fact that the ethyl acetyl compound,

$$C_6Cl_4(OC_2H_3O)O(C_2H_5O)C_6Cl_2O_2,$$

offered a great resistance to reducing agents, being entirely unaffected by those which reduced the mother substance.[1] We are unable to offer any explanation for this difference between these compounds on the basis of Formula II. On the other hand, Formula I (which has been proved incorrect) would account for it.

The methods of formation of the two substances also threw no light on their constitution; they are action of the alcohol on tetrachlor-*o*-quinone, or on the heptachlor hemiether, or on the hexachlor ether, $C_6Cl_4O_2C_6Cl_2O_2$. As already pointed

[1] It is possible that Dr. P. W. Carleton on one occasion got a reduction of the quinone oxygen atoms with phenylhydrazine, but this single preliminary observation needs confirmation before it can be accepted.

out, this last method of formation could be easily explained by Formula I, but since II has been proved to be the correct one, it is very surprising because most of the work done up to this time on the hexachlor ether has indicated that it is a very stable body, and yet here one of the bonds is broken by so weak a reagent as cold alcohol. We get here little help from analogy, as the only other ethers which we have been able to find in which two rings are bound together by two atoms of oxygen are those prepared by Hillyer,[1] in which he found one of the ether bonds could be broken by alkalies, but apparently did not try weaker reagents. We hope to study this subject more carefully in the near future.

EXPERIMENTAL PART

Action of Benzyl Alcohol on Tetrachlor-o-quinone

Heptachlor-o-quinopyrocatechin Hemiether, $(C_6Cl_4(OH)OC_6Cl_4O_2)_2C_6H_6$.—MacLaurin and one of us[1] obtained by the action of benzyl alcohol on tetrachlor-*o*-quinone at ordinary temperatures a yellow product melting at 215°, for which no probable formula could be found. On taking up again the study of this substance we prepared it (as before) by allowing a mixture of 20 grams of benzyl alcohol and 20 grams of the quinone to stand at ordinary temperature, when, after 24 hours, a yellow product was deposited which was purified by crystallization from a mixture of equal parts of benzene and ligroin until it showed the constant melting point, 215°. To get this melting, or rather decomposition, point constant, it is necessary to dip the tube containing the substance into a bath at 215°. If the specimen has been previously heated in the bath, it turns red and then melts at 290°–300°, the melting point of the compound

$$C_6Cl_4O_2C_6Cl_2O_2.$$

The benzyl alcohol mother liquors, if mixed with more quinone, gave a new supply of the yellow product, and this action could be continued many times. The secondary products of

[1] THIS JOURNAL, **23**, 125 (1900); **26**, 361 (1901).
[2] *Ibid.*, **38**, 165 (1907).

the reaction were hydrochloric acid and, to judge by the smell, benzaldehyde.

In properties this substance resembled the heptachlor-*o*-quinopyrocatechin hemiether discovered by P. W. Carleton and one of us,[1] as it decomposed at 215° (instead of 214°), and was easily converted by alcohol into the red ether,

$$C_6Cl_4O_2C_6Cl_2O_2.$$

The crystalline form, however, was different—hexagonal prisms instead of scales—and the analyses gave results not in harmony with this view of its composition.

	Calculated for $C_6Cl_4(OH)OC_6Cl_2O_2$	Calculated for $(C_6Cl_4(OH)OC_6Cl_2O_2)_2C_6H_6$	Found I	Found II	Found III
C	31.47	36.25	33.69	...	...
H	0.22	0.81	2.56	...	...
Cl	54.31	50.06	...	50.26	49.89

The formula with benzene of crystallization gives an excellent agreement between the percentages for chlorine, but not between those for carbon and hydrogen. We are of the opinion that the specimen used by Dr. MacLaurin for this combustion had lost part of its benzene, but we did not make another, as the presence of benzene of crystallization was sufficiently proved by the work that follows. The composition of the substance was confirmed by the following molecular-weight determination:

0.6442 gram substance in 20.69 grams C_6H_6 gave $\Delta = 0°.179$.

	Calculated for $C_6Cl_4(OH)OC_6Cl_2O_2$	Found
Mol. wt.	457.5	464

The substance was converted into the red ether

$$C_6Cl_4O_2C_6Cl_2O_2$$

easily by heat, but we hoped that by keeping the temperature low enough we might succeed in driving off the benzene before this reaction took place.

2.4135 grams of the substance dried *in vacuo*, after being heated to about 80° for several hours, lost 0.1776 gram. Al-

[1] This Journal, **30**, 499 (1908).

though the weight was not absolutely constant, it was necessary to stop the determination at this point, as further heating produced decomposition, shown by the appearance of a red color.

	Calculated for $(C_6Cl_4(OH)OC_6Cl_3O_2)_2C_6H_6$	Found
C_6H_6	7.86	7.36

To prove that this loss consisted of benzene, and was not due to decomposition attended by loss of hydrochloric acid, another specimen was heated at the same temperature, until it had lost 4.96 per cent., when two analyses gave the chlorine calculated on the substance dried *in vacuo* as 49.77 and 50.05 per cent. Since the compound $(C_{12}Cl_7O_4H)_2C_6H_6$ contains 50.06 per cent. chlorine there had been no loss of hydrochloric acid in this case. It would have been better to have analyzed the residue from the determination of the benzene, but this had been used to study the action of higher temperatures, and had shown that at 145° the red ether began to form in quantity, but the amount could not be determined, as a slight sublimation was observed.

The result given above was confirmed by the action of boiling water on the substance, which converted it into the red hexachlor-*o*-quinopyrocatechin ether without any other complex organic product except an amount of chloranilic acid too small to be determined. The weight of red ether formed was taken in two experiments:

I. 0.3239 gram substance gave 0.2780 gram of red ether; the loss was therefore 0.0459 gram.

II. 0.4258 gram substance gave 0.3601 gram red ether; the loss was therefore 0.0657 gram.

	Calculated for $(C_6Cl_4(OH)OC_6Cl_3O_2)_2C_6H_6$	Found I	Found II
$2HCl + C_6H_6$	15.21	14.17	15.43

The observed loss in each case corresponds as nearly as could be expected to that calculated for the reaction

$$(C_6Cl_4(OH)OC_6Cl_3O_2)_2C_6H_6 = 2C_6Cl_4O_2C_6Cl_2O_2 + 2HCl + C_6H_6.$$

In the earlier work by P. W. Carleton and one of us[1] a speci-

[1] This result was not published as it was supposed at that time to be a bad analysis.

men of the heptachlor-*o*-quinopyrocatechin hemiether (prepared by the action of equivalent quantities of tetrachlor-*o*-quinone and tetrachlorpyrocatechin in warm chloroform) was recrystallized from benzene instead of from chloroform, as usual, and on analysis gave the following result:

0.1858 gram substance gave 0.3780 gram AgCl.

	Calculated for $(C_6Cl_4(OH)OC_6Cl_3O_2)_2C_6H_6$	Found
Cl	50.06	50.29

This shows that the hemiether crystallizes with half a molecule of benzene, when that substance is present in its solution.

A small specimen of the substance prepared with benzyl alcohol was crystallized three times from ligroin, dried below 60°, and analyzed:

0.1039 gram substance gave 0.2256 gram AgCl.

	Calculated for $C_6Cl_4(OH)OC_6Cl_3O_2$	Found
Cl	54.31	53.70

Although this result leaves much to be desired, it is sufficiently good to prove that the product from benzyl alcohol is the heptachlor-*o*-quinopyrocatechin hemiether. The action of alcohol on the hemiether will be discussed later in this paper.

Heptachlor-o-quinopyrocatechin Monoacetylhemiether, $C_6Cl_4(OC_2H_3O)OC_6Cl_3O_2$.—This substance was made by MacLaurin and one of us[1] by the action of acetic anhydride on the product obtained from benzyl alcohol and tetrachlor-*o*-quinone, but in that case 58 per cent. of the hemiether was converted into the red ether, $C_6Cl_4O_2C_6Cl_2O_2$. We have found that the acetyl compound can be prepared without any formation of the red ether by boiling the hemiether with acetyl chloride instead of acetic anhydride for an hour in a flask with a return condenser. The yellow oil thus obtained was purified by crystallization from dilute alcohol or dilute acetic acid and gave the constant melting point 195° as before. We add the results of the analyses given in the previous paper compared with the theoretical percentage of chlorine.

[1] This Journal, **38**, 166 (1907).

	Calculated for $C_6Cl_4(OC_2H_3O)OC_6Cl_3O_2$	Found I	Found II
Cl	49.80	50.53	49.82

Properties of Heptachlor-o-quinopyrocatechin Monoacetylhemiether.[1]—Creamy white needles melting at 195° to a faint brown liquid. It is easily soluble in the commom organic solvents, from which it is deposited in an oily state. To obtain crystals dilute alcohol or dilute glacial acetic acid should be used. Strong hydrochloric acid has no action on it; it is moderately soluble in strong nitric acid; freely soluble in strong sulphuric acid or alkalies.

Heptachlordihydroxypyrocatechin Hemiether,

$$C_6Cl_4(OH)OC_6Cl_3(OH)_2$$

This substance was obtained by MacLaurin and one of us[2] by reducing the benzyl alcohol product with sulphurous dioxide. When zinc and acetic acid were used, the hexachlordihydroxypyrocatechin ether was formed. In taking up this work again we found it better to pass the sulphurous anhydride into a mixture of the benzyl alcohol product with one part of alcohol and three of water. The yellow color of the suspended solid changed soon to cream white, and if, as sometimes happened, part of the product was an oil, this solidified after standing for a short time. The product was filtered out, washed, allowed to dry and purified by crystallization from a mixture of benzene and ligroin. It was dried for an hour at 100°.

I. 0.1729 gram substance gave 0.3748 gram AgCl.

II. 0.1294 gram substance gave 0.2803 gram AgCl.

	Calculated for $C_6Cl_4(OH)OC_6Cl_3(OH)_2$	Found I	Found II	Found III
Cl	54.09	53.60	53.56	53.62

Number III is an analysis made by Dr. MacLaurin.

The molecular weight was determined by the boiling-point method.

1.4332 grams substance dissolved in 24.31 grams C_6H_6 gave Δ 0°.371.

	Calculated for $C_6Cl_4(OH)OC_6Cl_3(OH)_2$	Found
Mol. wt.	459.5	424

[1] THIS JOURNAL, **38**, 167 (1907).

[2] *Ibid.*, **38**, 168 (1907).

Properties of Heptachlordihydroxypyrocatechin Hemiether.—It crystallizes from a mixture of benzene and ligroin in grayish white, hexagonal prisms. The melting point was determined by MacLaurin and one of us as 188°–190°, the substance forming a black liquid. With no extraordinary precautions we did not get it above 181°–182°, but probably could have obtained the higher reading by dipping it into a bath at that temperature, instead of heating the tube in the bath in the usual way. This substance, in fact, is a most excellent example of the effect of varying conditions on these decomposition points, as, if kept for five minutes in a bath at 175°–176°, it melted at this point. It is freely soluble in all the common organic solvents except ligroin, in which it is almost insoluble. Most of these solutions deposit no crystals, but leave a glassy varnish on evaporation. Alcohol decomposes it, especially on warming, and the product was usually the hexachlordihydroxypyrocatechin ether, recognized by its appearance, melting point and solubilities. Strong hydrochloric acid had no effect on it; strong nitric acid, when warm, turns it red; strong sulphuric acid darkens it; sodic hydrate in aqueous solution shows a slight solvent action without change of color.

Heptachlordiacetoxypyrocatechin Acetylhemiether,

$$C_6Cl_4(OC_2H_3O)OC_6Cl_3(OC_2H_3O)_2$$

The heptachlordihydroxypyrocatechin hemiether was dissolved in acetic anhydride, and the solvent allowed to evaporate spontaneously. The dark green varnish obtained in this way was treated with a mixture of equal parts of benzene and alcohol, filtered from the undissolved portion and the filtrate mixed with 10–12 times its volume of alcohol; a precipitate which was formed in this way seemed to be the ether $C_6Cl_4O_2C_6Cl_2(OH)_2$. The filtrate from it yielded, on standing, white hexagonal crystals which were treated in the same way five more times, and then crystallized from benzene and methyl alcohol, when they showed the constant melting point 144° and were dried at 80° for analysis:

0.1278 gram substance gave 0.2204 gram AgCl.

	Calculated for $C_6Cl_4(OC_2H_3O)OC_6Cl_3(OC_2H_3O)_2$	Found
Cl	42.44	42.64

Properties of the Heptachlordiacetoxypyrocatechin Acetylhemiether.—White hexagonal prisms melting at 144° to a colorless liquid, which turns pale yellow at somewhat higher temperatures. It is soluble in ether, acetone, ethyl acetate or benzene, but no good crystals can be obtained from these solutions in the ordinary way. Strong hydrochloric acid, or nitric acid, or a solution of sodic hydroxide has no apparent action on it.

Hexachlormethoxy-o-quinopyrocatechin Hemiether,

$$C_6Cl_4(OH)—O—(CH_3O)C_6Cl_2O_2$$

(formerly called Hexachlor-*o*-quinomethylmonohemiacetal-pyrocatechin Ether)

This compound, which melts at 198° with decomposition, was discovered by MacLaurin and one of us[1] among the products formed by the action of methyl alcohol on tetrachlor-*o*-benzoquinone. It was also obtained by the action of methyl alcohol on a mixture of this quinone and the trichlormethoxy-*o*-quinonemonomethylhemiacetal,

$$C_6Cl_3(OCH_3)O(OCH_3OH),$$

melting at 138°–140°, or on the hexachlor ether,

$$C_6Cl_4O_2C_6Cl_2O_2.$$

P. W. Carleton and one of us added to these two new methods of preparation: (*a*) boiling the red ether, $C_6Cl_4O_2C_6Cl_2O_2$, with successive portions of methyl alcohol,[2] instead of letting the mixture stand at ordinary temperatures, and (*b*) treating the heptachlor hemiether, $C_6Cl_4(OH)OC_6Cl_2O_2$, with methyl alcohol. Most of the material used by us was prepared by this last method, and the one preceding it was also used successfully, but toward the end of our work we discovered a mode of preparing it which was better than any of those mentioned. It consisted in adding methyl alcohol to a mixture in molecular proportions of tetrachlorpyrocatechin and tetrachlor-*o*-quinone, when, after standing at ordinary temperatures for a few minutes, the red color of the solution became lighter, and yellow crystals of the compound appeared, which weighed

[1] This Journal, **38**, 150 (1907).
[2] *Ibid.*, **39**, 501 (1908).

as much as 50 grams, if 50 grams of the pyrocatechin, 50 grams of the *o*-quinone, and 150 grams of methyl alcohol were used. As an additional amount was obtained by concentration of the mother liquors, the yield was good, and the process took not more than 30 minutes. Another method, which is only of theoretical interest, consisted in treating the heptachlor hemiether with sodic methylate when, on acidifying the product with hydrochloric acid, the substance was obtained in a very pure state. Carleton and one of us[1] obtained the compound melting at 218° and containing two methyl groups by the action of sodic methylate on the hexachlor ether, $C_6Cl_4O_2C_6Cl_2O_2$, but we have not yet had time to find out what differences in the conditions led to this difference in the results.

Our substance, melting at 198°, was purified by crystallization from equal parts of benzene and ligroin. It was not analyzed, because the analysis and molecular-weight determinations made by Dr. MacLaurin had already established its composition.

Reduction of Hexachlormethoxy-o-quinopyrocatechin Hemiether—Hexachlormethoxy-o-dihydroxypyrocatechin Hemiether

$$C_6Cl_4(OH)\text{-}O\text{-}(CH_3O)C_6Cl_2(OH)_2$$

It was not easy to reduce this compound, as experiments with zinc and acetic acid or dilute hydrochloric acid in water, or methyl alcohol, either left the substance unaltered or gave the reduced ether, $C_6Cl_4O_2C_6Cl_2(OH)_2$, melting at 276°; sulphurous dioxide also was without action in aqueous or methyl alcohol solution, but we finally succeeded in obtaining a reduction product by the action of sulphurous dioxide and zinc dust. Ten grams of the finely divided substance were covered with 200 cc. of methyl alcohol, which dissolved most of the yellow solid, and diluted with 50 cc. of water, forming a finely divided precipitate. To the mixture a little zinc dust was added, and it was then heated on the steam bath and a stream of sulphurous dioxide passed through it, small quantities of zinc dust being dropped in from time to time. If the addition of the zinc dust was rapid enough, the heat generated made it

[1] THIS JOURNAL, **30**, 502 (1908).

unnecessary to warm on the steam bath. After 30 minutes the reduction was complete, and most of the product had dissolved. It was filtered hot and water added to the filtrate, which threw down a bulky white precipitate; this was filtered out, washed and, without drying, redissolved in hot methyl alcohol, and again precipitated with water and washed. If this treatment was omitted there was much trouble, in the crystallizations, from a viscous yellow body. The purification was carried out by crystallization from a mixture of benzene and ligroin until the substance melted with decomposition at 191°; the variation of this decomposition point under different conditions makes it of little value as a test of purity, and this was shown in a striking way by the fact that two specimens melted at this point, one of which had been crystallized three, the other seven times, and the first gave percentages of chlorine more than 0.60 per cent. below the theoretical, while those from the second specimen agree excellently with those calculated, as seen below. The specimen analyzed for carbon and hydrogen had been crystallized only three times. It was dried at 100°.

I. 0.2255 gram substance gave 0.2817 gram CO_2 and 0.0347 gram H_2O.

II. 0.1017 gram substance gave 0.1934 gram AgCl.

III. 0.1003 gram substance gave 0.1899 gram AgCl.

	Calculated for $C_6Cl_4(OH)O(CH_3O)C_6Cl_2(OH)_2$	Found I	II	III
C	34.29	34.07	...	...
H	1.31	1.72	...	...
Cl	46.79	...	47.02	46.81

These and several other analyses, which confirm them, leave no doubt of the composition of the substance.

I. Molecular-weight determination by the boiling-point method: 0.5866 gram substance in 13.16 grams ether gave Δ 0°.170 (k = 2110).

II. By the freezing-point method: 0.4193 gram substance in 20.59 grams nitrobenzene gave Δ 0°.313 (k = 7000).

	Calculated for $C_6Cl_4(OH)O(CH_3O)C_6Cl_2(OH)_2$	Found I	II
Mol. wt.	455	553	455

Properties of Hexachlormethoxy-o-dihydroxypyrocatechin Hemiether.—It crystallizes from a mixture of benzene and ligroin in long colorless needles. When heated up to its melting point under ordinary conditions, it melts at 191° to a colorless liquid, which turns brown and effervesces at higher temperatures, while at the same time a white sublimate is formed, which may be the unaltered substance, as a tendency to sublime, even at ordinary temperatures, was observed. If it is heated between 130° and 150° for 15 minutes, a grayish white substance is formed, which melts at 276° with blackening, and therefore is probably hexachlor-*o*-dihydroxypyrocatechin ether, $C_6Cl_4O_2C_6Cl_2(OH)_2$, which melts at this point. This view was confirmed by the fact that it is insoluble in benzene and only slightly soluble in alcohol, but on the other hand, although turned red by nitric acid, this change takes place less quickly than with the original compound. We tried to settle the question by the formation of the diacetyl compound, $C_6Cl_4O_2C_6Cl_2(OC_2H_3O)_2$, melting at 294°, but the amount of substance was too small for thorough purification, so we get no melting point above 282°. The reduction product is easily soluble in methyl or ethyl alcohol, ether, acetone, glacial acetic acid or benzene; nearly insoluble in ligroin. The best solvent for it is a mixture of benzene and ligroin. Cold, strong nitric acid gives a red color with it instantly; sulphuric acid produces apparently no effect; dilute alkalies dissolve its lightly, sometimes with a red color. Its alcoholic solution gives a green color with ferric chloride.

Hexachlormethoxy-o-diacetoxypyrocatechin Acetylhemiether,
$C_6Cl_4(OC_2H_3O)O(CH_3O)C_6Cl_2(OC_2H_3O)_2$

This substance was obtained by dissolving the reduced substance melting at 191°, just described, in glacial acetic acid saturated with sodic acetate, adding an excess of acetyl chloride and boiling for 6 hours under a return condenser. The product was precipitated with water and recrystallized from hot methyl alcohol until it showed the constant melting point 128°–129°, which needed five crystallizations:

I. 0.1137 gram substance gave 0.1684 gram AgCl.

II. 0.1240 gram substance gave 0.1843 gram AgCl.

	Calculated for $C_6Cl_4(OC_2H_3O)O(CH_3O)C_6Cl_2(OC_2H_3O)_2$	Found I	Found II
Cl	36.66	36.62	36.75

Properties of the Hexachlormethoxy-o-diacetoxypyrocatechin Acetylhemiether.—It crystallizes well from hot methyl alcohol in rather short white needles, melting at 128°–129°. It is soluble in all the common organic solvents except ligroin, but good crystals could be obtained and a viscous impurity removed only with methyl alcohol. A strong acid or sodic hydroxide seems to be without immediate action upon it, but probably decomposes it by long heating.

In our attempts to find a method to prepare the substance just described two other compounds were obtained when the boiling was carried on for not more than two hours. One of these was extremely soluble in all solvents except water and ligroin. By crystallization from ligroin white needles were obtained, or if a little benzene was present diamond-shaped plates, which melted at 122°.

I. 0.1609 gram substance gave 0.3157 gram AgCl.

II. 0.1340 gram substance gave 0.2623 gram AgCl.

	Found I	Found II
Cl	48.51	48.40

These results agree with the percentage of chlorine in

$$C_6Cl_4(OH)O(HO)C_6Cl_2(OH)_2,$$

which is 48.31, and this might have been formed by the hydrochloric acid given off in the reaction, after all the sodic acetate had been converted into sodic chloride, but, as we see no reason why this hydroxyl compound should not have been converted into an acetyl derivative, we do not feel inclined to assign this formula to the substance without further work, for which we had no time, as it lay outside of the field of our research.

The third compound obtained from this reaction crystallized in large rhombic plates from a mixture of benzene and ligroin and melted at 186°–188°.

0.1132 gram substance gave 0.1946 gram AgCl.

	Calculated for $C_6Cl_4(OH)O(CH_3O)C_6Cl_2(OC_2H_3O)(OH)$	Found
Cl	42.86	42.51

As this monoacetyl compound would be a natural product of the reaction when the boiling lasted only two hours, we feel no hesitation in assigning this composition to it on a single analysis.

Properties of Hexachlormethoxy-o-monoacetoxyhydroxypyrocatechin Hemiether.—It forms large rhombic plates, which melt at 186°–188°. It is only slightly soluble in alcohol or benzene; less so in ligroin. Neither of the three strong acids nor sodic or ammonic hydroxide has a perceptible action on it at ordinary temperatures. As nitric acid does not convert it into the yellow *o*-quinoacetyl hemiether, it is fair to suppose that the acetyl group is attached to one of the oxygen atoms of the dichlorpyrocatechin, and not to the oxygen of the hemiether.

Hexachlorethoxy-o-quinopyrocatechin Hemiether,

$$C_6Cl_4(OH)O(C_2H_5O)C_6Cl_2O_2$$

This substance was prepared by MacLaurin and one of us[1] by the action of ethyl alcohol on tetrachlor-*o*-quinone in the cold for two weeks, or on hexachlor-*o*-quinopyrocatechin ether[2] for two months. We have improved the latter process by using boiling instead of cold alcohol. The red ether was boiled with 20 times its weight of alcohol for 15 minutes in a flask with a return condenser, and the boiling with fresh quantities of alcohol for fifteen minutes was continued until the ether had disappeared, which usually happened in two or three hours. The hot solutions were poured into a dish, and, as the liquid cooled, crystals were deposited which were filtered out and with an additional crop, obtained by evaporation of the mother liquors, were washed with alcohol and then crystallized from a mixture of equal volumes of benzene and alcohol, as this converted any red ether that had escaped

[1] THIS JOURNAL, **38**, 159 (1907).

[2] This ether can be made conveniently by a method found by Dr. H. A. Flint, to work well with the corresponding bromine compound. The equivalent quantities of tetrachlor-*o*-quinone and tetrachlorpyrocatechin were dissolved separately in alcohol instead of glacial acetic acid, mixed together, and water added cautiously, until a slight permanent precipitate was formed. On standing for 2 hours a heavy precipitate of the ether was thrown down, which was purified by boiling it with a small quantity of benzene, as this dissolved the ethyl derivative, the chief impurity, without taking up any considerable amount of the ether.

action into the ethyl derivative (Anaylses I and II). The substance was also purified, although less advantageously, by crystallization from a mixture of equal parts of benzene and ligroin. In order to obtain the decomposition point of 210°, as in the previous work, the substance must be dipped into the hot bath; if only heated rapidly, it is hard to raise its melting point above 206°.

Two new methods of preparation found by us were inprovements on those just described. (*a*) The heptachlor-*o*-quinopyrocatechin hemiether was treated with cold alcohol, when the solid at first dissolved, but after standing from one to five minutes the solution deposited a red precipitate, recognized as the hexachlor-*o*-quinopyrocatechin ether by its properties, which was converted into the ethyl compound by repeated boilings with fresh quantities of alcohol, as described above. The filtrates on cooling gave crystals, or with water a yellow precipitate, which was purified by crystallization from benzene and ligroin (Analyses III and IV).

(*b*) Tetrachlorpyrocatechin and tetrachlor-*o*-quinone in molecular proportions were dissolved separately in ethyl alcohol, the solutions mixed, and allowed to stand, when after two hours a crystalline precipitate had formed consisting partly of the red ether, $C_6Cl_4O_2C_6Cl_2O_2$, and partly of the ethyl compound. This was boiled under a return condenser with a mixture of 9 parts of alcohol and one of benzene, the liquid being poured off from time to time, and replaced by a fresh portion, or by the mother liquors from the ethyl compound formed in the earlier stages of the process. As the red ether is insoluble in this mixture, only the ethyl compound was removed, and the process was continued until all the red ether had been converted into the ethyl compound by the boiling alcohol. This process is the best, if the materials are pure, but the impurities usually contained in the tetrachlor-*o*-quinone (which is too unstable to be purified advantageously) exert an unfavorable effect on this reaction, so that the preparation from the heptachlor compound is on the whole the best.

I. 0.1469 gram substance gave 0.2716 gram AgCl.
II. 0.1802 gram substance gave 0.3325 gram AgCl.
III. 0.1377 gram substance gave 0.2537 gram AgCl.
IV. 0.1507 gram substance gave 0.2770 gram AgCl.

	Calculated for $C_6Cl_4(OH)O(C_2H_5O)C_6Cl_2O_2$	Found I	II	III	IV
Cl	45.61	45.69	45.60	45.54	45.44

The analyses made by Dr. MacLaurin of this substance gave the following results:

	Calculated	Found		
C	35.97	36.34	36.31	.....
H	1.28	1.47	1.60	.....
Cl	45.61	45.82	45.72	45.83

As we had reason to think our determinations of the molecular weight would give a different result from that previously obtained by the boiling-point method, we have used the freezing-point method, which gives much more trustworthy results than the former under the unfavorable conditions to which our work was exposed:

I. 0.4080 gram substance dissolved in 20.82 grams C_6H_6 gave Δ 0°.193.

II. 0.3081 gram substance dissolved in 28.15 grams C_6H_6 gave Δ 0°.118.

	Calculated for $C_6Cl_4(OH)O(C_2H_5O)C_6Cl_2O_2$	Found I	II
Mol. wt.	467	497	455

As these results were confirmed by determinations of the molecular weight of the acetyl compound, they supersede those given by MacLaurin and one of us.

A quantitative study of the reaction between alcohol and the heptachlor hemiether, which was made for another purpose, showed that the yield of the compound $C_6Cl_4O_2C_6Cl_2O_2$ was 89 per cent., that of very crude compound

$$C_6Cl_4(OH)O(C_2H_5O)C_6Cl_2O_2$$

67 per cent. of those required by the reaction

$$(C_6Cl_4(OH)OC_6Cl_3O_2)_2C_6H_6 + C_2H_5OH = C_6Cl_4O_2C_6Cl_2O_2 + C_6Cl_4(OH)O(C_2H_5O)C_6Cl_2O_2 + 2HCl + C_6H_6.$$

Of the products of secondary reactions there were recognized chloranilic acid and tetrachlorpyrocatechin.

There is little to be added to the description of the properties of hexachlorethoxy-*o*-quinopyrocatechin hemiether given already.[1] The lemon-yellow rhombic plates are obtained from benzene, or a mixture of benzene and ligroin; while from alcohol, or alcohol and benzene, it crystallizes in hexagonal prisms. When heated for some time to 170°, it turns red; it melts between 200° and 210° according to the speed of heating, but it is hard to get the conditions necessary to raise its melting point above 206°. When heated with strong hydrochloric acid in a sealed tube at 105° for 3 hours, a red solid was formed, which appeared to contain the ether $C_6Cl_4O_2C_6Cl_2O_2$, the reduced ether, chloranilic acid, and apparently several other compounds, forming a mixture too complex to study in the time at our disposal. At 160° a black mass was obtained, from which nothing but tetrachlorpyrocatechin has been obtained. This was recognized by its melting point, solubilities and reaction with ferric chloride.

Hexachlorethoxy-o-quinopyrocatechin Acetylhemiether,

$$C_6Cl_4(OC_2H_3O)O(C_2H_3O)C_6Cl_2O_2$$

This substance, melting at 195°, was prepared by the action of acetic anhydride, as previously described,[2] in order to redetermine the molecular weight, since we had reason to believe that the earlier determination was misleading. For greater security both the freezing-point (I) and boiling-point (II) methods were used:

I. 0.5042 gram substance dissolved in 23.81 grams C_6H_6 gave Δ 0°.242 (k = 5100).

II. 0.5900 gram substance dissolved in 23.76 grams C_6H_6 gave Δ 0°.111 (k = 2670).

	Calculated for $C_6Cl_4(OC_2H_3O)O(C_2H_3O)C_6Cl_2O_2$	Found I	Found II
Mol. wt.	509	429	597

In order to obtain a good result by the boiling-point method under the conditions existing in our organic laboratory, the

[1] Jackson and MacLaurin: THIS JOURNAL, **38**, 160 (1907).
[2] *Ibid.*, **38**, 160 (1907).

following precautions were necessary. The lower part of the tube containing the substance was filled with glass beads and several small pieces of platinum. The bulb of the thermometer was contained in a glass tube slightly greater in diameter than the bulb, the lower end of which rested on the glass beads, while the upper extended a few mm. above the surface of the liquid, and thus protected the bulb of the thermometer from the cooler liquid falling from the condenser. The whole apparatus was enclosed in paper, so that only the thermometer projected into the room. This is the most important of these precautions, as without the paper envelope the boiling points in various trials differed by an amount corresponding to more than half the molecular weight of the compound, thus explaining the incorrect results obtained by this method in some of the earlier work on this subject. With these arrangements, however, fairly constant boiling points were observed.

Attempts to reduce this acetyl compound with zinc and acetic acid, zinc and hydrochloric acid, or sulphurous dioxide in alcohol, or in alcohol and water, produced no change in the cold, and, when the mixture was heated, either no change or the formation of the ether $C_6Cl_4O_2C_6Cl_2(OH)_2$.

Reduction of Hexachlorethoxy-o-quinopyrocatechin Hemiether with Sulphurous Dioxide—Hexachlorethoxy-o-dihydroxypyrocatechin Hemiether,

$C_6Cl_4(OH)O(C_2H_5O)C_6Cl_2(OH)_2$

Two grams of the ethyl compound, finely powdered and suspended in 150 cc. of a mixture of 3 parts of alcohol to one of water, were submitted to the action of a stream of sulphurous dioxide at about 70°. At the end of 3 hours yellow crystals, probably of the compound $C_6Cl_4O_2C_6Cl_2(OH)_2$, had appeared in small quantity, and the solution was poured off and mixed with water, which formed a white flocculent precipitate consisting of the reduction product with traces of the unaltered substance and of the compound $C_6Cl_4O_2C_6Cl_2(OH)_2$, while the filtrate was strongly colored with chloranilic acid. After washing the precipitate it was extracted with hot 60 per cent.

alcohol, which did not dissolve the yellow crystals, and the filtrate was precipitated with water, and purified by repeated solution in alcohol (3 to 1) and precipitation with water to free it from chloranilic acid, followed by crystallization from mixtures of benzene and ligroin, and of benzene and alcohol, until it melted at 173°, when it was dried at 80°.

I. 0.1466 gram substance gave 0.2669 gram AgCl.
II. 0.1184 gram substance gave 0.2157 gram AgCl.
III. 0.0996 gram substance gave 0.1817 gram AgCl.

	Calculated for $C_6Cl_4(OH)O(C_2H_5O)C_6Cl_2(OH)_2$	Found I	II	III
Cl	45.39	45.04	45.07	45.09

Properties of Hexachlorethoxy-o-dihydroxypyrocatechin Hemiether.—It crystallizes from benzene in white, poorly defined needles, sometimes showing a tint of cream, and melts at 173° to a colorless liquid, which turns brown and then black as the temperature rises above this point. It is soluble in alcohol, ether, ethyl acetate, benzene or glacial acetic acid; insoluble in water. Strong hydrochloric acid or sulphuric acid produces no apparent effect; nitric acid turns it red; aqueous ammonic hydroxide turns it gray and dissolves it slightly; aqueous sodic hydroxide dissolves it more freely with no change of color. Acetic anhydride, whether hot or cold, or hot acetyl chloride, gave with it a product which was apparently hexachlordiacetoxypyrocatechin ether, but by the modification of the process described below the triacetyl compound was obtained.

Hexachlorethoxy-o-diacetoxypyrocatechin Acetylhemiether,
$C_6Cl_4(OC_2H_3O)$–O–$(C_2H_5O)C_6Cl_2(OC_2H_3O)_2$

The reduced substance, $C_6Cl_4(OH)O(C_2H_5)OC_6Cl_2(OH)_2$, melting at 173°, was dissolved in glacial acetic acid, saturated with sodic acetate, and an excess of acetyl chloride added to the cold solution, which formed a heavy precipitate of sodic chloride. The mixture was then heated on the steam bath under a return condenser for two hours, the excess of acetyl chloride present being enough to insure boiling at a low temperature, after which it was allowed to cool and poured slowly into a

large volume of water. The white precipitate thus formed was washed, dried and crystallized from a mixture of alcohol and benzene till it showed the constant melting point 165°, when it was dried at 80°.

I. 0.1153 gram substance gave 0.1662 gram AgCl.
II. 0.1136 gram substance gave 0.1637 gram AgCl.

	Calculated for $C_6Cl_4(OC_2H_3O)O(C_2H_3O)C_6Cl_2(OC_2H_3O)_2$	Found I	Found II
Cl	35.78	35.66	35.66

Properties of Hexachlorethoxy-o-diacetoxypyrocatechin Acetylhemiether.—It forms white, long, flat crystals and melts at 165°. It is freely soluble in ethyl acetate, glacial acetic acid or benzene; slightly soluble in alcohol, less so in ligroin. The best solvent is a mixture of alcohol and benzene. Each of the three strong acids or sodic hydroxide appears to have no action upon it in the cold.

Reduction of Hexachlorethoxy-o-quinopyrocatechin Hemiether with Zinc and Acetic Acid.—This reaction yielded MacLaurin and one of us[1] long silky needles melting at 247°, which were not studied further. In taking up this work again we proceeded as follows: Two grams of the finely powdered substance were suspended in about 100 times their weight of glacial acetic acid, granulated zinc added, and the mixture warmed gently on the steam bath, enough water being added gradually to establish an effervescence. The reduction usually lasted about half an hour, and after this the hot solution, which had changed from orange to colorless, was allowed to cool, when white needles separated; it was then added to cold water, which threw down a white flocculent precipitate that was washed till free from zinc salts. In our first experiment this precipitate, after several crystallizations from acetic acid and water, melted at 249°, and was undoubtedly identical with the substance melting at 247°, previously obtained, but unfortunately it was decomposed in drying it for analysis, and in all our later experiments the product, after crystallization from benzene and ligroin, melted at 276°, when heated

[1] THIS JOURNAL, **38**, 163 (1907).

as usual, but the melting point was raised to 288° if the substance was dipped into the hot bath. It seemed to be therefore the hexachlor-*o*-dihydroxypyrocatechin ether,

$$C_6Cl_4O_2C_6Cl_2(OH)_2,$$

which was found by MacLaurin and one of us to melt at 290°. This inference was confirmed by the following analyses:

I. 0.1018 gram substance gave 0.2073 gram AgCl.
II. 0.1072 gram substance gave 0.2163 gram AgCl.

	Calculated for $C_{12}Cl_6O_4H_2$	Found I	Found II
Cl	50.36	50.36	49.89

Acetic anhydride acting in the cold on this reduction product gave a white substance, which was purified by solution in nitrobenzene and precipitation with ligroin, followed by one crystallization from benzene and ligroin, when it melted at 251°. It was dried at 100°:

I. 0.1048 gram substance gave 0.1936 gram AgCl.
II. 0.1399 gram substance gave 0.2580 gram AgCl.

	Calculated for $C_6Cl_4O_2C_6Cl_2(OC_2H_3O)(OH)$	Found I	Found II
Cl	45.81	45.68	45.58

It appears, therefore, that a monoacetyl derivative was formed instead of the diacetyl compound, and that this is the usual result with cold acetic anhydride was shown by obtaining it from a specimen of the compound $C_6Cl_4O_2C_6Cl_2(OH)_2$, made in the usual way.

Properties of Hexachlor-o-hydroxyacetoxypyrocatechin Ether.— It forms white needles from nitrobenzene, glistening white needles from benzene. Upon heating it turns black and melts at 251°. It is soluble in nitrobenzene; slightly soluble in alcohol, glacial acetic acid or benzene (one part in about 200); still less soluble in the other organic solvents. Strong sulphuric acid reddens it, whereas no change is visible when it is treated with strong hydrochloric acid, or nitric acid, or an aqueous solution of sodic hydroxide.

If the acetic anhydride was boiled under a return condenser with the dihydroxy ether instead of allowing it to act in the

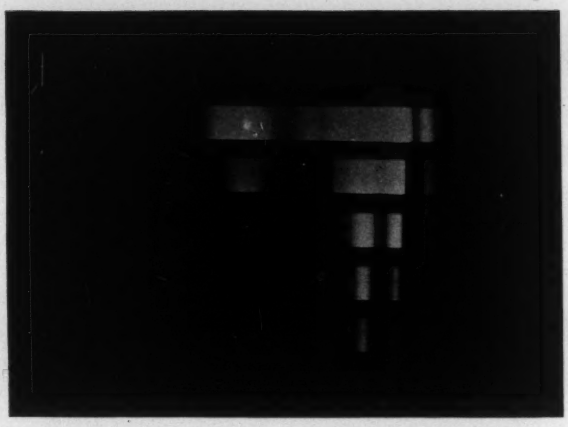


Plate I—Nettle Chlorophyllan

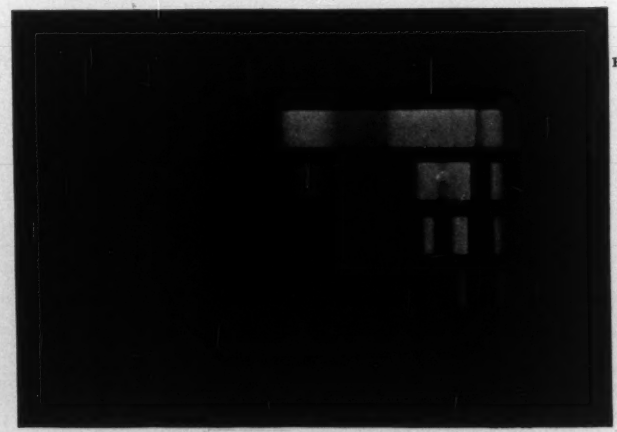


Plate II—*Acer negundo* Chlorophyllan

cold, white plates of the diacetoxy derivative described by MacLaurin and one of us were obtained. We found in this case a higher melting point, 294°, than that observed previously, 282°, but, as the substance blackens between 260° and 270°, such a difference in observations is not unnatural. The identity of our product and that prepared by Dr. MacLaurin is proved by the following analyses of a product purified by extraction with boiling and washing with cold benzene:

I. 0.1417 gram substance gave 0.2411 gram AgCl.

II. 0.1349 gram substance gave 0.2283 gram AgCl.

	Calculated for $C_6Cl_4O_2C_6Cl_2(OC_2H_3O)_2$	Found I	Found II
Cl	42.01	42.07	41.85

The research will be continued.

CAMBRIDGE, MASS.
Sept. 9, 1911

ON THE DUALITY OF CHLOROPHYLL AND THE VARIABLE RATIO OF THE TWO CONSTITUENTS

BY C. A. JACOBSON AND L. MARCHLEWSKI

It has long been known that chlorophyll, the green coloring matter in leaves, is not a chemical entity but a mixture of two substances. The two components are called chlorophyll and allochlorophyll.[1]

Among the experimenters who have taken cognizance of these two coloring matters in higher plants are Stokes,[2] Sorby,[3] Marchlewski and Schunck,[4] and Tswett.[5]

A great deal of conjecture has been expressed regarding the relative amounts of the two substances present in leaves, Tswett[6] maintaining the view that the two are always present in the ratio of 1 : 5, while Sorby[7] believes that this ratio

[1] L. Marchlewski: "Die Chemie der Chlorophylle," Braunschweig, 1909.
[2] P. Roy. Soc., **21**, 442 (1873).
[3] *Ibid.*, **21**, 442 (1873).
[4] J. Chem. Soc., **77**, 1080 (1900).
[5] Ber. d. chem. Ges., **41**, 1352 (1908).
[6] *Loc. cit.*
[7] *Loc. cit.*

is changeable, but up to the present experimental evidence has been too meager to permit of drawing any definite conclusions. It should be said that Marchlewski and Marszalek,[1] by a study of the chlorophyllans of nettle and *Acer platanoides* leaves, have also come to the conclusion that the ratio of chlorophyll to allochlorophyll in these species is not a constant one.

Since each one of the substances has a long series of known derivatives, it was manifestly of great importance to settle the question whether the ratio of chlorophyll to allochlorophyll is a constant or variable quantity in the same and different species of plants, and if this ratio changes with change of conditions under which the plant grows.

In order that erroneous deductions may not be drawn from the words chlorophyll and chlorophyllan, each of which has a double meaning at present, we suggest that the prefix *neo* be added to the words in question when they mean the chemical individuals, and that the original names be allowed to represent the mixtures of the two coloring matters in the ratio in which they exist in the plant. Thus chlorophyll represents the natural mixture of neochlorophyll and allochlorophyll, and chlorophyllan the natural mixture of neo- and allochlorophyllan. This slight modification of the nomenclature will simplify the discussion and prevent ambiguity.

In the present paper we offer four distinct lines of evidence in support of our contention that the ratio of chlorophyll to allochlorophyll varies with different species of plants and also with changing conditions of growth of the same species.

First. The actual amount of allochlorophyllan, the nearest acid derivative of allochlorophyll, isolated from a given weight of *Acer platanoides* chlorophyllan of different years is very different.

Second. The absorption bands in the visible spectrum of the chlorophyllans obtained from different species by identical methods differ considerably.

Third. The chlorophyllan absorption bands in the ultraviolet part of the spectrum also differ for different species.

Fourth. The extinction coefficients, in monochromatic light,

[1] Biochem. Z., **35**, 413 (1911).

Plate III—*Platanus occidentalis* Chlorophyllan

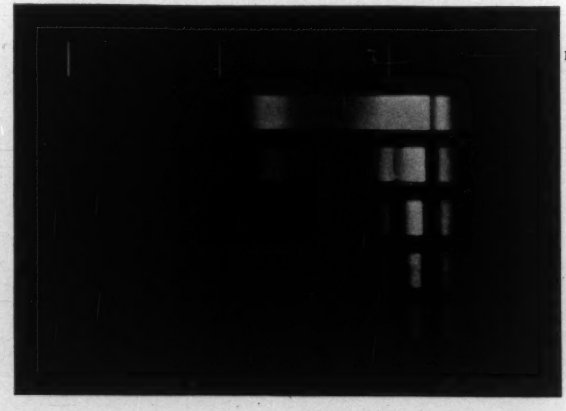


Plate IV—Pure Allochlorophyllan

of equally concentrated solutions of chlorophyllans from different species vary considerably.

The results of our experiments will be recorded in the foregoing order without further reference to the divisions.

From the work of Marchlewski and Marszalek,[1] it was learned that the 1910 *Acer platanoides* leaves obtained from Russian Poland yielded a chlorophyllan from which 28.7 per cent. of allochlorophyllan could be isolated, the method of Marchlewski and Malarski[2] being used.

Last summer another lot of the same kind of *Acer* leaves was obtained from the same region and the chlorophyllan isolated by exactly the same method, but in this case only 3.1 per cent. of allochlorophyllan could be obtained. The summer of 1910 was very dry in that particular region, while last summer was a wet one.

We also had available some of the 1910 nettle chlorophyllan and compared it spectroscopically with last summer's product, finding that the former contained a great deal less allochlorophyllan than the latter. It may be noted that the summer of 1911 in Western Galicia was particularly dry and sunny. From these two instances it would appear that the climatic conditions play an important role in the production of the one or the other component of chlorophyll.

For the present investigation, the following varieties of leaves were available: *Acer ps-platanus*, *Acer platanoides*, *Acer campestre*, *Platanus occidentalis*, *Isatis tinctoria*, *Acer ps-platanus purpurascens*, *Acer dasycarpum* and two different lots of *Acer negundo*, besides the chlorophyllans from alfalfa, nettle and *Galeopsis tetrahyt*. All the above varieties of leaves, with the exception of the *Acer platanoides* and alfalfa, were gathered last summer from trees in the botanical gardens of the Cracow University, the alfalfa having been brought from the Nevada Agricultural Experiment Station farm.

The two coloring matters were not studied in the original form in which they exist in the leaves, but as the nearest derivative obtained by treating them with a weak acid. In

[1] *Loc. cit.*
[2] Biochem. Z., **31**, 529 (1909).

other words, we converted the neo- and allochlorophyll present in the alcoholic extract into neo- and allochlorophyllan. This mixture was obtained from each lot of leaves in exactly the same manner, as follows: The dried and finely powdered leaves were treated with an equal weight of 95 per cent. boiling alcohol, well stirred and allowed to stand for half an hour, after which the alcoholic extract was pressed out under 300 atmospheres, filtered and treated with a 10 per cent. alcoholic solution of oxalic acid, in the proportion of one part of acid to fifteen parts of extract. The solution was then well stirred and allowed to stand overnight. The following morning the precipitated chlorophyllan was filtered, washed with alcohol, and reprecipitated from a concentrated chloroform solution according to the method of E. Schunck[1] for the precipitation of phylloxanthine.

The chlorophyllans were then dried to constant weight, first in a hot-water oven and then in a vacuum desiccator over sulphuric acid. Solutions in chloroform were prepared of all the chlorophyllans obtained by the foregoing method. The solutions were all made of equal strength, 1 cc. containing 0.0004 gram. The colors of the solutions thus obtained were not identical. They ranged from a dark olive-green in the case of the nettle and *Acer campestre* to a brownish red in the case of *Acer negundo*. The intermediate colors corresponded to those obtained by mixing solutions of the varieties mentioned.

Not only was there a difference in the solutions to the naked eye, but when looked at through the spectroscope, a marked difference appeared in the region of the fourth and fifth absorption bands, located in the green part of the spectrum. In the case of the olive-green solutions, the fourth band was narrower than the fifth, the latter being broad and well pronounced, whereas the fourth band in the brownish red solution (*Acer negundo*) was broad and strong while the fifth was too faint to be measured, although a scarcely perceptible shadow appeared in this region.

[1] P. Roy. Soc., **50**, 303 (1891).

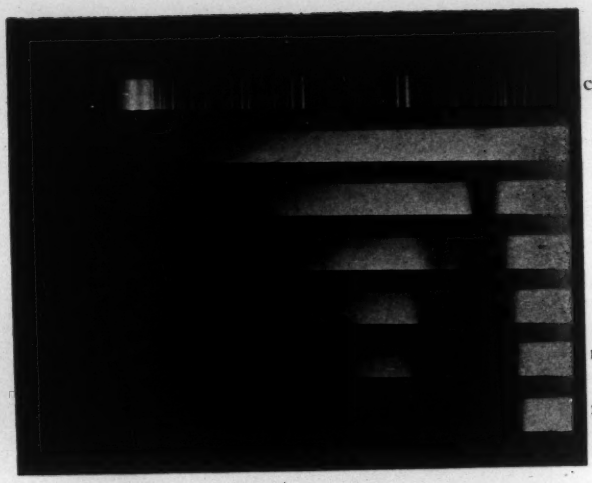


Plate VII—Pure Allochlorophyllan

Plate VIII—*Platanus occidentalis* Chlorophyllan

Table I.—Spectrum of Chlorophyllan from Nettle Leaves (1910)

Concentration, 1 cc. ($CHCl_3$) = 0.0004 gram

Thickness of layer	1 mm.	3 mm.	5 mm.	7 mm.	10 mm.
Band I	λ680.0–654.0	682.8–648.0	687.0–644.5	690.0–641.5	697.5–637.3
Band II	614.6–597.0	615.1–598.4	617.2–593.5	619.5–592.4	621.7–589.7
Band III	.....	567.7–557.5	569.8–556.2	571.2–555.5	574.8–554.3
Band IV	540.4–530.8	542.1–530.8	542.3–530.2	544.1–529.0	545.6–524.4
Band V	512.3–498.2	512.7–496.8	514.3–493.5	516.2–494.3	518.8–489.9

According to their intensity the bands may be placed in the following order: I > V > IV > II > III

Table II.—Spectrum of Chlorophyllan from Acer negundo *Leaves*

Concentration, 1 cc. ($CHCl_3$) = 0.0004 gram

Thickness of layer	1 mm.	3 mm.	5 mm.	7 mm.	10 mm.
Band I	λ672.6–650.5	677.6–645.0	681.0–640.1	684.0–637.8	686.5–634.5
Band II	605.5–593.5	608.7–592.4	609.2–591.2	613.4–590.0	616.8–585.5
Band III	564.3–556.2	568.4–556.8	569.1–556.8	573.0–554.3	575.5–552.2
Band IV*a*	540.4–532.5	540.7–531.3	542.3–518.0	545.0–511.8	548.5–493.1
Band IV*b*	525.4–521.7	526.7–519.3			
Band V	trace	trace	trace		

Order of intensity: I > IV*a* = IV*b* > II > III > V

Table III.—Spectrum of Chlorophyllan from Platanus occidentalis *Leaves*

Concentration, 1 cc. ($CHCl_3$) = 0.0004 gram

Thickness of layer	1 mm.	3 mm.	5 mm.	7 mm.	10 mm.
Band I	λ682.3–651.5	683.5–643.5	684.0–641.6	684.6–638.3	688.3–635.4
Band II	603.8–594.7	609.7–595.5	611.7–592.0	616.0–589.7	617.3–587.5
Band III	.....	565.7–557.5	568.2–555.3	571.0–551.8	573.7–551.3
Band IV	531.1–532.2	538.6–533.7	542.5–530.0	543.2–527.2	447.3–493.3
Band V	....	510.7–499.6	512.7–495.7	513.7–495.0	

Order of intensity: I > IV = V > II > III

The fourth and fifth bands in the solution of *Platanus occidentalis* chlorophyllan were about equally strong. These differences will also appear from Tables I–III, where the measured absorption bands of nettle, *Acer negundo* and *Platanus occidentalis* chlorophyllans are recorded in wave lengths. These three varieties were chosen because the nettle and *Acer negundo* chlorophyllans represent the two extremes, while that of the *Occidentalis* is a close mean between them.

A comparison of the figures given in the above tables will show, further, that the positions of the first band are not identical in the three varieties. This cannot be detected except in very dilute solutions. The wave lengths for Band I in the 1 mm. layer were found to be for

Nettle chlorophyllan	680.0–654.0$\mu\mu$
Acer negundo chlorophyllan	672.6–650.5$\mu\mu$
Platanus occidentalis chlorophyllan	682.3–651.5$\mu\mu$

The band of the *Acer negundo* chlorophyllan is shifted slightly towards the more refrangible part of the spectrum and is accompanied by a shading on the less refrangible side. The *Acer negundo* chlorophyllan spectrum differs from the other two in still another way, namely, the fourth band is double in very dilute solutions and the measurements are thus recorded for the 1 and 3 mm. layers.

Photographs of the chlorophyllan spectra of these three varieties were taken in the visible portion, with the helium spectrum added above for reference. These are shown in Plates I–III, but the difference in the region of the fourth and fifth bands above alluded to is not apparent for the reason that our photographic plates (Panchromatic B, Wainwright and Wratten, Croydon), were least sensitive to the green wave lengths. A striking confirmation of this fact will come out when we discuss the extinction coefficients of the three varieties in monochromatic light.

A direct comparison of the *Acer negundo* chlorophyllan with the pure allochlorophyllan prepared according to the method of Marchlewski and Malarski[1] shows a close resemblance between the two. One is led to suppose that the chloro-

[1] *Loc. cit.*

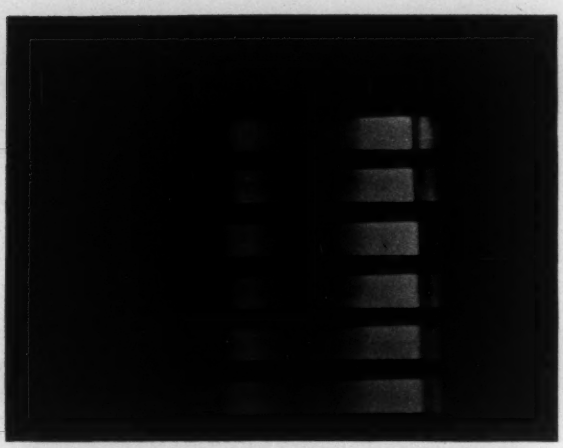


Plate V—Six Different Chlorophyllans

a. Pure Allochlorophyllan
b. *Acer negundo* Chlorophyllan
c. Nettle Chlorophyllan
d. *Occidentalis* Chlorophyllan
e. Mixture of *a* and *c*
f. Alfalfa Chlorophyllan

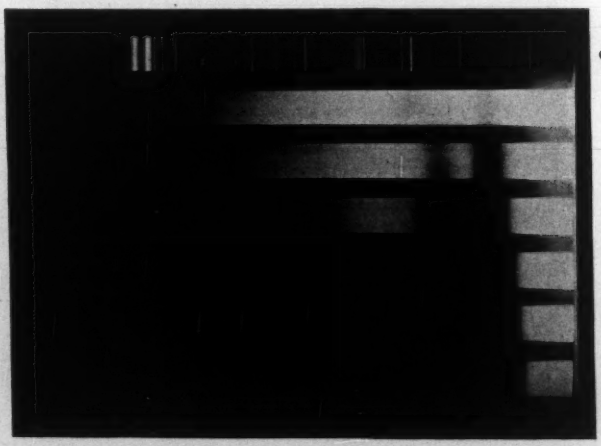


Plate VI—*Acer negundo* Chlorophyllan

phyllan from *Acer negundo* leaves is composed chiefly of allochlorophyllan. Plate IV represents the visible spectrum of pure allochlorophyllan.

After repeated trials we were able to obtain a photograph of several varieties of chlorophyllan on the same plate (V) that shows the shifting of the first band with reference to the second helium line. Here also is seen the similarity between the *Acer negundo* chlorophyllan and the pure allochlorophyllan. The *Platanus occidentalis* chlorophyllan appears identical with the mixture prepared from equal parts of nettle and allochlorophyllan, while the alfalfa shows a preponderance of the neochlorophyllan over the allochlorophyllan.

The ultraviolet spectrum is perhaps even more illustrative of the great difference in the composition of the chlorophyllans of these varieties. By first considering that of the *Acer negundo* chlorophyllan, Plate VI, it will be seen that there are three distinct absorption bands, the broadest and strongest of which is at the less refrangible and the weakest at the more refrangible end. The positions of these bands are ascertained in correlation to the lines of the copper spectrum. Plate VII represents the absorption bands of the pure allochlorophyllans and again it is seen that there is a very close similarity between these two. All the photographs taken in the ultraviolet were of more dilute solutions, 5 cc. of the chloroform solutions, previously described, being diluted to 50 cc., and the six photographs shown on each plate are of layers of 2, 4, 6, 8, 10 and 12 mm. thickness.

In the following tables are given the wave lengths of the three absorption bands of *Acer negundo* and of pure allochlorophyllan as measured on the negatives:

Table IV.—Spectrum of the Acer negundo *Chlorophyllan*

Thickness of layer mm.	Band IV	Band III	Band II	Band I
2	.....	Too indistinct	.....	436.5–442.8
4	.....	to allow of	411.3–419.2	433.5–446.4
6	.....	measure-	410.0–421.3	431.1–450.3
8	370.8–377.1	ment	407.0–422.3	427.2–454.2
10	369.0–379.0		404.8–422.9	424.9–455.6
12	367.3–380.0		401.7	457.3

Order of intensity: I > II > IV > III

Table V.—Spectrum of Pure Allochlorophyllan

Thickness of layer mm.	Band IV	Band III	Band II	Band I
2	.....		.....	437.0–443.7
4	.....	Absent	412.7–420.5	433.3–447.7
6	367.7–376.6		410.0–423.0	431.3–451.2
8	366.2–378.4		409.2–424.3	429.2–454.8
10	364.3–379.2		408.0–425.4	427.0–456.8
12	362.7–380.3		406.7	458.5

Order of intensity: I > II > IV

From the above measurements it is seen that the two sets of wave lengths are in close agreement with one another, with the exception of the more refrangible side of Band IV of the allochlorophyllan, which it is scarcely possible to differentiate.

A comparison of these values with those given in the paper by Marchlewski and Malarski[1] will reveal the fact that there is a discrepancy between the two sets of readings. It should be said that this discrepancy is due to the difference in solvents used. By a direct control it was shown that an ethereal solution, which was then employed, displaces the absorption bands to that extent in the direction of the more refrangible end.

The allochlorophyllan spectrum (Plate VII) does not show a band between the second and fourth, although a trace of a band appears there on the *Acer negundo* plate. The band just referred to comes out distinctly on the *Platunus occidentalis* plate (VIII), and is stronger and more pronounced still on Plate IX, representing the nettle chlorophyllan. On the latter plate it is also seen that Band I is narrow and faint, while Band II is very strong. Bands I and II are about equally strong on Plate VIII, showing, as did the visible spectrum, that the *Platanus occidentalis* chlorophyllan contains about equal quantities of neo- and allochlorophyll. From the four plates just described it would appear that Bands I and IV are due to allochlorophyllan, while Band III is due to neochlorophyllan, Band II being common to both.

In the following tables will be found the wave lengths of

[1] *Loc. cit.*

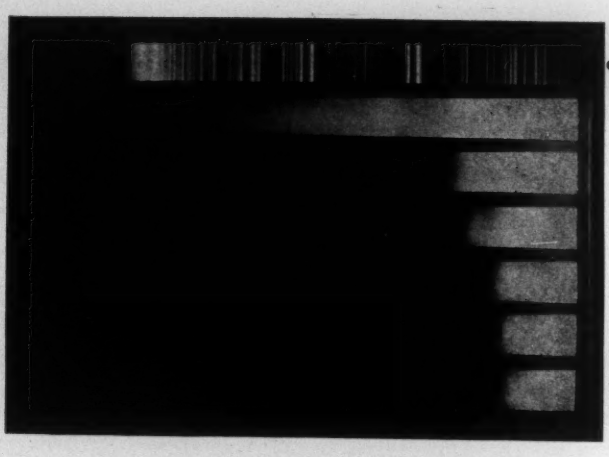


Plate IX—Nettle Chlorophyllan (1910)

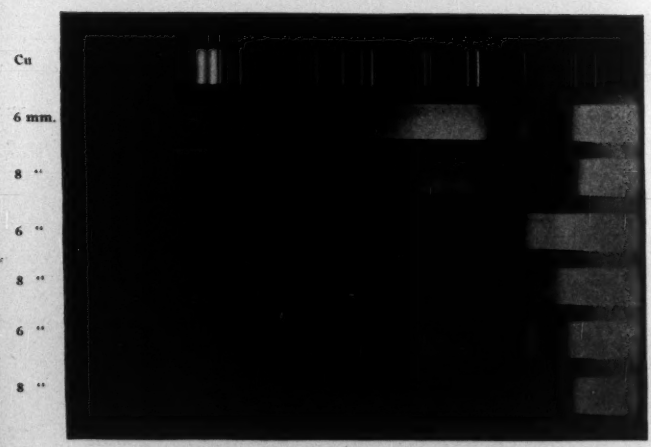


Plate X—Three Different Chlorophyllans

a. *Acer negundo* Chlorophyllan
b. Nettle Chlorophyllan (1910)
c. *Platanus occidentalis* Chlorophyllan

the absorption bands as measured on the negatives of the *Platanus occidentalis* and nettle chlorophyllans:

Table VI.—Spectrum of the Chlorophyllan from Platanus Occidentalis

Thickness of layer mm.	Band IV	Band III	Band II	Band I
2	.....	.....	415.4–419.2	437.5–444.3
4	.....	.....	410 2–422.6	436.5–445.9
6	366.8–376.8	391.8–399.7	408.3–423.1	434.7–447.3
8	364.8–378.1	389.7–400.7	405.5–425.7	432.8–449.6
10	362.9–378.6	387.8	426.5	430.9–452.3
12	358.6–379.0	384.2	.....	455.2

Order of intensity: I = II > IV > III

Table VII.—Spectrum of the Chlorophyllan from 1910 Nettle

Thickness of layer mm.	Band IV	Band III	Band II	Band I
2	.....	407.0	421.6	.....
4	357.8–376.7	404.8	423.4	433.4–442.7
6	365.0–377.8	389.2	424.8	431.9–443.2
8	362.3–381.6	384.8	426.2	430.7–443.7
10	358.8–382.8	383.7	427.9	429.7–445.0
12	350.7			446.8

Order of intensity: II > III > IV > I

The characteristic differences in the spectra of these three varieties become even more apparent when they are placed in juxtaposition on one negative, as has been done on Plate X. The two layers nearest the copper lines are from the *Acer negundo* chlorophyllan, the next two from nettle and the last two from *Platanus occidentalis*. The photograph is self-explanatory.

Still another method was available for showing the variable ratio of the two green coloring matters in leaves, namely, the extinction coefficient of the different solutions in monochromatic light. As was mentioned in the early part of the discussion, the solutions containing a preponderance of allochlorophyllan show but a faint fifth band in the visible part of the spectrum, which grows more and more pronounced as the percentage of neochlorophyllan increases.

By combining the monochrometer with the König-Mar-

ten spectrophotometer, we were able to produce a beam of light which scarcely varied $4\mu\mu$ on either side of $\lambda = 505$, which is the center of the fifth band in the visible spectrum. The solutions of *Acer negundo*, nettle (1910) and *Platanus occidentalis* chlorophyllan were diluted with an equal volume of chloroform and introduced in the apparatus mentioned, a 10 mm. layer being used in each case.

For *Acer negundo* chlorophyllan.

$\alpha_1 = 159.24$. $\alpha_2 = 17.44$

$$\Sigma = \frac{\log \tan \frac{\alpha_1}{2} - \log \tan \frac{\alpha_2}{2}}{1/d \text{ (cm.)}}$$

$\therefore \Sigma = 3.10$ (extinction coefficient)

For nettle chlorophyllan:

$\alpha_1 = 167.5$. $\alpha_2 = 10.34$

$\therefore \Sigma = 4.01$ (extinction coefficient)

For *Platanus occidentalis* chlorophyllan:

$\alpha_1 = 163.80$. $\alpha_2 = 13.92$

$\therefore \Sigma = 3.51$ (extinction coefficient)

These experiments again show that *Platanus occidentalis* chlorophyllan occupies an intermediate position between the *Acer negundo* and nettle chlorophyllan.

The above research establishes without a doubt that the components of chlorophyllan, and consequently of chlorophyll, in different varieties of plants have no constant ratio.

In order to anticipate a criticism regarding the influence the solvents might exert on the chlorophyllan of the different varieties of leaves we carried out the following experiment:

An alcoholic extract of some (1911) *Acer platanoides* leaves was prepared, and it was found that its extinction coefficient for sodium light was 14.12. An alcoholic solution of (1911) nettle leaves was diluted with alcohol until its extinction coefficient was approximately that of the *platanoides*, or 14.30.

From 1 liter of each of these solutions were obtained the corresponding chlorophyllans in exactly the same way, i. e., they were both precipitated with 25 cc. of oxalic acid solu-

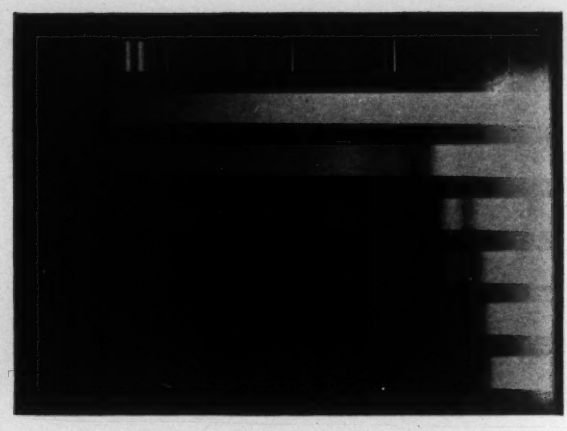


Plate XI—Nettle Chlorophyllan (1911)

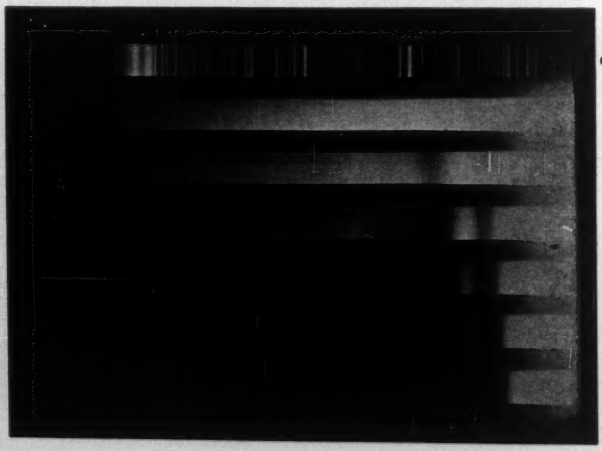


Plate XII—*Acer platanoides* Chlorophyllan (1911)

tion, washed with the same volume of alcohol, taken up in 25 cc. of chloroform, which was evaporated to 4 cc., and 30 cc. of 96 per cent. alcohol added to each one. Two hundred and twenty-five cc. of alcohol was used to wash each one, the chlorophyllans were dried in the same way, and solutions of equal concentrations prepared and photographed. The bands on the two plates were identical as far as we could make out, showing that the components existed in the same proportion in the two chlorophyllans. Now, if, on altering the volume of the solvents in the two cases beyond the limits of procedure for the preparation of any of the foregoing chlorophyllans, the photographs still showed the components in the same ratio, we would be justified in concluding that the solvents have no influence. Consequently, equal amounts of the two chlorophyllans were taken and the *platanoides* chlorophyllan precipitated from twice the volume of chloroform used in the first case, while the nettle chlorophyllan was precipitated from one-eighth of the former volume of chloroform by three times the volume of alcohol. The chlorophyllans thus obtained were filtered, dried, and solutions of equal concentration prepared. Photographs of these solutions were also taken in the ultraviolet, which shows that the bands still maintain the same relative intensity. Plate XI represents the nettle and Plate XII the *Acer platanoides* chlorophyllan. Plate XI also shows that the nettle of last summer contains more allochlorophyllan than the nettle of 1910, which is shown on Plate IX.

The four lines of evidence herein presented are thus seen to be in perfect accord with one another, and establish with absolute certainty that a variable ratio exists between the constituents of chlorophyll in different species of plants, ranging all the way from almost pure allochlorophyll in the case of *Acer negundo* to almost pure neochlorophyll in the case of nettle, and that this ratio varies in the same species of plants, depending on climatic conditions.

[Contributions from the Sheffield Laboratory of Yale University]

CXCVII.—THIOAMIDES

THE ACTION OF HYDROGEN SULPHIDE ON NITROGEN-SUBSTITUTED AMINOACETONITRILES

By Treat B. Johnson and Gerald Burnham

[FOURTH PAPER]

In their last paper on thioamides of amino acids, the writers[1] described the behavior of aminoacetonitrile[2] (I) towards hydrogen sulphide. They showed that the nitrile reacts normally with this reagent, forming, by addition, the corresponding thioamide (II). This compound, however, was not isolated. It was extremely unstable and underwent, in an alcoholic solution and at ordinary temperature, an unique condensation and was transformed into thioglycylglycinethioamide (III), with evolution of ammonia. This thiopolypeptide derivative, being also unstable, then lost another molecule of ammonia and condensed to dithiopiperazine (IV), the sulphur analogue of diacipiperazine (V), which was first described by Curtius.[3] In fact, this cyclic compound (IV) was the chief product of the reaction. These transformations are represented as follows:

$$\underset{\text{I}}{NH_2CH_2CN} \longrightarrow \underset{\text{II}}{NH_2CH_2CSNH_2} \longrightarrow$$

$$\underset{\text{III}}{NH_2CH_2CSNHCH_2CSNH_2} \longrightarrow \underset{\text{IV}}{NHCH_2CSNHCH_2CS}$$

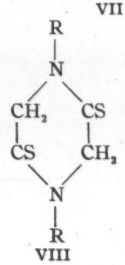
$$\underset{\text{V}}{NHCH_2CO.NH.CH_2.CO}$$

This formation of a dithiopiperazine by the condensation of a thioamide of an α-amino acid is a new reaction, which is of great biological significance. It is not improbable that sulphur compounds of this character may functionate in the synthesis of sulphur proteins from simpler substances. Therefore it was of special interest and importance to determine whether

[1] J. Biol. Chem., **9**, 449.
[2] Klages: Ber. d. chem. Ges., **35**, 1514.
[3] Curtius and Göbel: J. prakt. Chem., [2] **37**, 173.

this property of condensing to cyclic compounds is characteristic of the different types of thioamides, which contain the common nucleus $-NH-\overset{|}{\underset{|}{C}}CSNH_2$. The chief aim of the work described in this paper was to decide whether thioamides of nitrogen-substituted amino acids (type VII) would undergo similar transformations as the thioamide of glycocoll and be converted into the corresponding substituted dithiopiperazines (VIII).[1]

$$\underset{\text{VI}}{R.NHCH_2CN} \longrightarrow \underset{\text{VII}}{R.NHCH_2CSNH_2} \longrightarrow$$



VIII

In order to obtain secondary thioamides of the type under discussion, we selected for examination the following six derivatives of aminoacetonitrile, NH_2CH_2CN, viz.:

1. Phenylaminoacetonitrile,[2] $C_6H_5NH.CH_2CN$.
2. *p*-Tolylaminoacetonitrile,[3] $CH_3C_6H_4NHCH_2CN$.
3. Anisoylaminoacetonitrile, $CH_3OC_6H_4CONHCH_2CN$.
4. Hippuronitrile,[4] $C_6H_5CONHCH_2CN$.
5. Carbethoxyaminoacetonitrile,[5] $C_2H_5OOC.NHCH_2CN$.
6. Glycoluronitrile or the nitrile of hydantoic acid,[6] $NH_2CO.NH.CH_2CN$.

[1] This study of thioamides of amino acids is one of a projected series on sulphur compounds, which has been planned for this laboratory.—T. B. J.

[2] Knoevenagel: Ber. d. chem. Ges., **37**, 4081. Bucherer and Schwalbe: *Ibid.*, **39**, 2800.

[3] Knoevenagel and Bucherer: *Loc. cit.*

[4] Klages: J. prakt. Chem., **65**, 190. Klages and Haack: Ber. d. chem. Ges., **36**, 1646.

[5] Johnson and McCollum: THIS JOURNAL, **65**, 67.

[6] Bailey: *Ibid.*, **28**, 391.

These six nitriles all combined smoothly with hydrogen sulphide, forming the corresponding thioamides, viz., phenylaminoacetothioamide, $C_6H_5NHCH_2CSNH_2$, tolylaminoacetothioamide, $CH_3C_6H_4NHCH_2CSNH_2$, anisoylaminoacetothioamide, $CH_3OC_6H_4CONHCH_2CSNH_2$, hippurothioamide, $C_6H_5CONH.CH_2CSNH_2$, carbethoxyaminoacetothioamide,

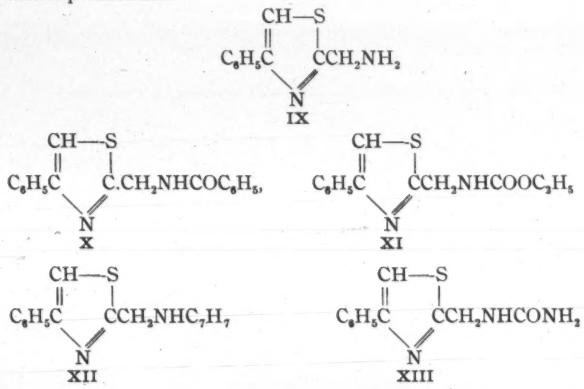
$$C_2H_5OOCNHCH_2CSNH_2,$$

and glycolurothioamide, $NH_2CONHCH_2CSNH_2$, respectively. It is remarkable with what ease hydrogen sulphide adds to this series of nitriles and, in fact, the nitriles of all amino acids which we have so far examined. With the above nitriles the addition of hydrogen sulphide was apparently almost instantaneous at ordinary temperature and in most cases the pure thioamides began to separate from the ammoniacal solutions within a few minutes after passing in hydrogen sulphide gas.

We now find that these six thioamides are stable compounds and can be heated in alcoholic solution without any apparent change. When heated above the temperature of their melting points they are decomposed with evolution of hydrogen sulphide and other volatile products. We obtained no evidence, in any case, of the formation of a dithiopiperazine (VIII), or a thiopolypeptide derivative. These results are especially interesting when one considers the fact that glycinethioamide, $NH_2CH_2CSNH_2$, undergoes spontaneously, at ordinary temperature, this condensation, forming dithiopiperazine. Whether secondary thioamides (VII), in which R represents a strongly positive grouping, will be found to be less stable and condense as glycinethioamide must be decided by further work.

In the course of our work we have also examined the behavior of four of our thioamides towards bromoacetophenone, $C_6H_5COCH_2.Br$, viz., hippurothioamide, carbethoxyaminoacetothioamide, tolylaminoacetothioamide and glycolurothioamide. They reacted smoothly with this halide, in alcohol, forming the corresponding thiazoles, viz., α-phenyl-μ-benzoylaminomethylthiazole (X), α-phenyl-μ-carbethoxyaminomethylthiazole (XI), α-phenyl-μ-tolylaminomethylthiazole (XII), and

α-phenyl-μ-carbamylaminomethylthiazole (XIII), respectively. They are all characteristic, crystalline compounds and are derivatives of the hitherto unknown thiazole base, α-phenyl-μ-aminomethylthiazole (IX), which theoretically should be formed by the action of bromoacetophenone on glycinethioamide, $NH_2CH_2CSNH_2$. This base (IX) was obtained in the form of its dihydrobromide by hydrolysis of α-phenyl-μ-carbethoxyaminomethylthiazole (XI) with hydrobromic acid. Thiazole bases of this type, corresponding to benzylamine in the aromatic series, are apparently unknown and the writer intends to give a description of their chemical behavior in a future publication.



EXPERIMENTAL PART

Hippurothioamide, $C_6H_5CO.NH.CH_2.CSNH_2$.—An excellent yield of this thioamide can be obtained by the action of hydrogen sulphide on hippuronitrile.[1] One part of the nitrile, finely pulverized, is suspended in about seven parts of strong alcoholic ammonia and hydrogen sulphide then conducted into the alcohol at 0° until it is completely saturated. The nitrile dissolves completely under these conditions and the thioamide generally begins to deposit in a short time. After

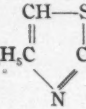
[1] *Loc. cit.*

standing for a few hours the amide is filtered off and the filtrate allowed to evaporate spontaneously, when more of the same substance is always obtained. We obtained from 42, 50 and 30 grams of the nitrile 35, 45 and 25.6 grams, respectively, of the pure thioamide. The compound is insoluble in ether and crystallizes from alcohol in beautiful, transparent blocks, which melt at 150° with slight effervescence. Analyses (Kjeldahl):

	Calculated for $C_9H_{10}ON_2S$	Found I	Found II
N	14.43	14.06	14.23

Action of Bromoacetophenone on Hippurothioamide

α-Phenyl-μ-benzoylaminomethylthiazole,



C_6H_5C $CCH_2NHCOC_6H_5$.—Two grams of hippurothioamide were dissolved in the smallest possible volume of hot absolute alcohol, 1.5 grams of bromoacetophenone added, and the solution digested on the steam bath for about 2.5–3 hours. On cooling, this thiazole separated in clusters of colorless needles which melted at 145° to an oil. It was purified by crystallization from alcohol and separated, on slow cooling, in rosettes of needles, which melted at 148°. The yield of purified material was one gram. Analyses (Kjeldahl):

	Calculated for $C_{17}H_{14}ON_2S$	Found I	Found II
N	9.52	9.22	9.24

Carbethoxyaminoacetothioamide, $C_2H_5OOCNH.CH_2.CSNH_2$.—This thioamide was prepared from carbethoxyaminoacetonitrile, which has been described in a previous paper from this laboratory.[1] Thirty grams of the nitrile were dissolved in 200 cc. of strong alcoholic ammonia and hydrogen sulphide passed into the solution at 0° until it was saturated. The thioamide is quite soluble in alcohol and only 6.5 grams separated from the solution. The remainder separated after evaporation of the alcohol at ordinary temperature. This

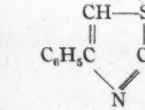
[1] Johnson and McCollum: *Loc. cit.*

compound is insoluble in ether and soluble in benzene. It crystallized from alcohol in characteristic, rectangular blocks, which melt at 118° to an oil without effervescence. The yield of pure thioamide was 23.1 grams, or 61 per cent. of the theoretical. Analyses (Kjeldahl):

	Calculated for $C_5H_{10}O_2N_2S$	Found I	Found II
N	17.28	17.20	17.01

The Action of Bromoacetophenone on Carbethoxyaminoacetothioamide

α-Phenyl-μ-carbethoxyaminomethylthiazole,

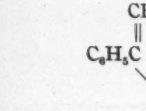


C_6H_5C $CCH_2NHCOOC_2H_5$.—Five grams of this thioamide were dissolved in a small volume of absolute alcohol, 6.2 grams of bromoacetophenone added, and the solution digested on the steam bath for about 6–7 hours. Hydrogen sulphide was slowly evolved during the digestion. After cooling, a small amount of yellow material separated and was identified as sulphur. The alcohol solution was concentrated and cooled, when a thick oil was obtained which finally crystallized. This substance was insoluble in hot benzene, soluble in cold 95 per cent. alcohol and ethyl acetate, insoluble in cold water, and melted under warm water to an oil which solidified again, on cooling, and melted at about 45°. The compound was purified by digestion with benzene and was obtained in the form of needles, which melted at 145°–150° with effervescence. On recrystallizing this same substance from water or dilute alcohol the melting point was lowered to 75°. On digesting this again with benzene the melting point was raised to 145° with effervescence. The properties of the compound, and the fact that it contained bromine, indicated that we were dealing with an unstable hydrobromide of the above thiazole. The yield of pure material was 3.5 grams. Analyses (Kjeldahl):

	Calculated for $C_{12}H_{14}O_2N_2S.HBr$	Found I	Found II
N	8.16	8.30	8.28

In order to obtain the free base, the above salt was dissolved in hot alcohol and water added to the hot solution until an oil separated. On cooling this finally crystallized and melted at 53°–56° to a clear oil without effervescence. In order to remove every trace of bromine this substance was digested again with water, when the pure base was finally obtained. It crystallized in prisms and melted at 59°–61° to an oil. The base is extremely soluble in the common organic solvents. Analyses (Kjeldahl):

	Calculated for $C_{12}H_{14}O_2N_2S$	Found I	Found II
N	10.68	10.53	10.31

α-Phenyl-μ-aminomethylthiazole Hydrobromide,  .—Six grams of the preceding carbethoxythiazole hydrobromide were digested with 25 cc. of hydrobromic acid, on the sand bath, for 3 hours. On cooling, the above salt separated in prismatic, colorless crystals, which melted at 253° with strong effervescence. The salt was soluble in cold alcohol and water, insoluble in benzene and glacial acetic acid. It was purified by recrystallization from hydrobromic acid and the melting point remained constant at 253°. The yield was 5.0 grams. Analysis (Kjeldahl):

	Calculated for $C_{10}H_{10}N_2S.2HBr$	Calculated for $C_{10}H_{10}N_2S.HBr$	Found
N	7.96	10.33	7.99

Anisoylaminoacetonitrile, $CH_3OC_6H_4CONHCH_2CN$.—This nitrile was prepared by dissolving the sulphate of aminoacetonitrile[1] in water and shaking with the required proportions of potash and anisoyl chloride. It crystallized from alcohol in thin, transparent plates, which melted at 153°–154° to a clear oil without effervescence. The yield was good. Analyses (Kjeldahl):

	Calculated for $C_{10}H_{10}O_2N_2$	Found I	Found II
N	14.23	14.56	14.45

[1] Klages: *Loc. cit.*

Anisoylaminoacetothioamide, $CH_3OC_6H_4CO.NHCH_2.CSNH_2$.—From 7 grams of the preceding nitrile we obtained 6 grams of this thioamide. It was purified by crystallization from hot alcohol and separated, on cooling, in slender prisms which melted at 189° with effervescence. Analyses (Kjeldahl):

	Calculated for $C_{10}H_{12}O_2N_2S$	Found I	Found II
N	12.52	12.38	12.50

Phenylaminoacetothioamide, $C_6H_5NH.CH_2CSNH_2$.—This thioamide was prepared by the action of hydrogen sulphide on phenylaminoacetonitrile. The latter compound was made according to Bucherer and Schwalbe's[1] directions from formaldehyde, sodium bisulphite, aniline and potassium cyanide. The compound was purified by crystallization from 95 per cent. alcohol and separated in stout blocks which melted at 166° to a brown oil with effervescence. Analysis (Kjeldahl):

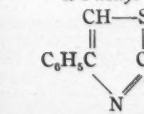
	Calculated for $C_8H_{10}N_2S$	Found
N	16.86	16.93

p-Tolylaminoacetothioamide, $CH_3C_6H_4NHCH_2CSNH_2$.—From tolylaminoacetonitrile[2] and hydrogen sulphide. We obtained 49.8 grams of the pure thioamide from 50 grams of the nitrile. It was purified for analysis by crystallization from alcohol and deposited, on slow cooling, in beautiful, rhombic plates or tabular prisms, which melted at 152° to an oil with only slight effervescence. Analysis (Kjeldahl):

	Calculated for $C_9H_{12}N_2S$	Found
N	15.55	15.33

The Action of Bromoacetophenone on Tolylaminoacetothioamide

α-Phenyl-μ-tolylaminomethylthiazole,



$C_6H_5C \quad CCH_2NHC_6H_4CH_3$

$\quad\quad N$

.—Seven grams of this thioamide and one molecular proportion of bromoacetophenone (7.8

[1] Ber. d. chem. Ges., **39**, 2796.

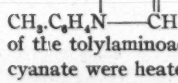
[2] Bucherer and Schwalbe: *Loc. cit.*

grams) were dissolved in alcohol and the solution digested on the steam bath for 3 hours. We obtained a red solution, which was then evaporated to dryness to remove all the alcohol. The product obtained here was a viscous liquid which showed no tendency to crystallize on cooling. It was triturated with dilute sodium hydroxide solution to neutralize hydrobromic acid and the oil then dissolved in ether, dried over calcium chloride and the ether finally allowed to evaporate spontaneously. The free thiazole was obtained under these conditions as a crystalline solid which was very soluble in ether and benzene. It was purified for analysis by recrystallization from ligroin. It separated from this solvent in light brown prisms which melted at 109°–111° to a red oil without effervescence. The compound separates from alcohol in prisms which melt at 110°–111°. Analyses (Kjeldahl):

	Calculated for $C_{17}H_{16}N_2S$	Found	
		I	II
N	10.00	10.10	10.14

The Action of Phenyl Isothiocyanate on p-*Tolylaminoacetonitrile*

1-Phenyl-2-thio-3-tolyl-5-phenylthioureadihydroglyoxaline,



.—Nine and six-tenths grams of the tolylaminoacetonitrile and 9.0 grams of phenyl isothiocyanate were heated together at 100°. There was apparently an immediate reaction, a thick red syrup was obtained, and after heating for about one hour this completely solidified. This was then heated for one hour longer to thoroughly complete the reaction. The substance was purified by recrystallization from 95 per cent. alcohol and glacial acetic acid and deposited, on cooling, in bright yellow needles, which melted at 201° to an oil, with slight effervescence. The yield of purified material was 3.3 grams. It was dried for analysis at 100°.

Nitrogen determination (Dumas method):

I. 0.1805 gram substance gave 22.6 cc. N at 22° and 762 mm. pressure.

Sulphur determinations (Carius method):

I. 0.2743 gram substance gave 0.3083 gram $BaSO_4$.

II. 0.2737 gram substance gave 0.3078 gram $BaSO_4$.

	Calculated for $C_{32}H_{20}N_4S_2$	$C_{16}H_{12}N_2S$	Found I	II
N	13.46	14.94	13.8	.....
S	15.38	11.38	15.49	15.44

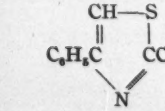
Glycolurothioamide (*Thioamide of Hydantoic Acid*), $NH_2CONHCH_2CSNH_2$.—Ten and five-tenths grams of the nitrile of hydantoic acid[1] were suspended in 100 cc. of strong alcoholic ammonia, and hydrogen sulphide conducted into the alcohol solution at 0°. The nitrile dissolved quickly under these conditions and within a few minutes the thioamide began to separate. After complete saturation with hydrogen sulphide the mixture was allowed to stand overnight and the thioamide then filtered off. The yield was 9.5 grams. It crystallizes from 95 per cent. alcohol, in which it is difficultly soluble, in colorless prisms which melt at 190°–191° with strong effervescence. The thioamide can also be recrystallized from water. Analyses (Kjeldahl):

	Calculated for $C_3H_7ON_3S$	Found I	II
N	31.57	31.80	31.32

This thioamide is a weak acid and dissolves in cold dilute sodium hydroxide solution without decomposition. On acidifying the solution with hydrochloric acid the original thioamide separated and melted at 190°–191°.

The Action of Bromoacetophenone on Glycolurothioamide

α-Phenyl-μ-carbamylaminomethylthiazole,



C_6H_5C (CH—S ‖ |) $CCH_2.NHCONH_2$; C—N.—Three and five-tenths grams of the thioamide were suspended in 40 cc. of absolute alcohol,

[1] *Loc. cit.*

5.2 grams of bromoacetophenone added, and the mixture heated on the steam bath. There was an immediate reaction; a clear solution was soon obtained and finally a crystalline substance began to separate from the hot solution. This was identified as the hydrobromic acid salt of the above thiazole. After heating about 2 hours the reaction was complete. The yield of salt was 5.0 grams and it melted without further purification at 210° with effervescence. The salt underwent dissociation when dissolved in water or 95 per cent. alcohol, but crystallized from dilute hydrobromic acid in colorless prisms which melted at 214° with effervescence. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{11}ON_2S.HBr$	Found
N	13.37	13.13

The free base was obtained by trituration of this salt with dilute alkali. It was purified by crystallization from 95 per cent. alcohol, and separated in beautiful, slender needle-like prisms, which melted at 190° without effervescence. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{11}ON_2S$	Found
N	18.03	17.94

NEW HAVEN, CONN.
December 11, 1911

[Contributions from the Sheffield Laboratory of Yale University]

CXCVIII.—HYDANTOINS

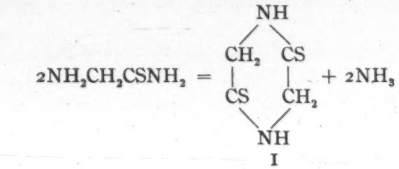
THE ACTION OF POTASSIUM THIOCYANATE ON PYRROLIDONECARBOXYLIC ACID. 2-THIOHYDANTOIN-4-PROPIONIC ACID

BY TREAT B. JOHNSON AND HERBERT H. GUEST

[TENTH PAPER]

This paper is a contribution to our knowledge of 2-thiohydantoins. The study of this class of cyclic compounds is one of a projected series of investigations on the nature of sulphur combinations in proteins which are now in progress in this laboratory.

In a previous paper from this laboratory the writer[1] has discussed evidence which supports the assumption that there are other sulphur combinations in proteins besides the cystein and cystin groups. The surmise that thioamide groupings —CS.NH— may be present or functionate in the synthesis of sulphur proteins from simpler substances led us to investigate the action of hydrogen sulphide on the nitrile of glycocoll, viz., aminoacetonitrile.[2] It was found that the thioamide of glycocoll was formed as expected, but we furthermore made the very interesting observation that this amide undergoes spontaneously an inner condensation, forming the prototype of a new class of piperazines, viz., dithiopiperazine (I), an anhydride of a thiopolypeptide. In connection with



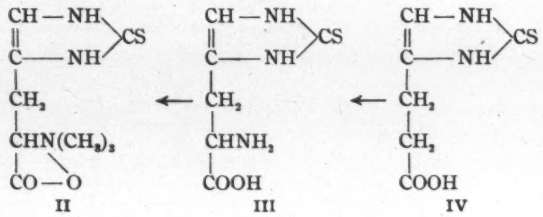
I

this work on thiopolypeptide derivatives we also took up the investigation of nitrogen-unsubstituted thiohydantoins. These represent a new class of thiohydantoins and a knowledge of their properties was considered very desirable because it seemed not improbable that such cyclic sulphur groupings might also functionate in the natural synthesis of proteins. In our last paper on hydantoins, the writer emphasized the importance of this cyclic grouping.[3]

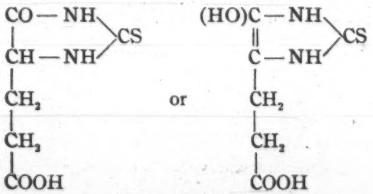
It is now very gratifying to learn, during the progress of our work, that our original assumption, that the thioamide grouping —CS.NH— probably functionates in the synthesis of proteins, has been attested independently by other investigators. Barger and Ewin,[4] for example, have made the interesting observation that the base *Ergothioneine*, $C_9H_{15}O_2N_3S$,

[1] Johnson: J. Biol. Chem., **9**, 439.
[2] Johnson and Burnham: *Ibid.*, **9**, 449.
[3] Johnson: *Ibid.*, **11** (1912).
[4] J. Chem. Soc., **1911**, 2336.

which Tanret[1] isolated from ergot, possesses the properties of a thioglyoxaline and is very probably the betaine of β-[2-mercaptoglyoxaline]-α-aminopropionic acid or β-[2-thiodihydroglyoxaline]-α-aminopropionic acid (II). So far as the writer is aware, this is the first case in which it has been shown that sulphur exists in nature in the form of a thioamide grouping. Ergothioneine, therefore, is a derivative of the unknown β-[2-mercaptoglyoxaline]-propionic acid (IV) and the latter may be viewed as a reduction product of the 2-thiohydantoin of glutaminic acid. These interesting relationships are represented by the following structural formulas:



II III IV



V

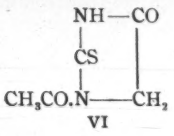
We shall now describe the synthesis of this hitherto unknown 2-thiohydantoin derivative of glutaminic acid, which is so closely related to this unique sulphur base.

In the first place, our attempts to synthesize this thiohydantoin (V) directly from glutaminic acid have been unsuccessful. The cycle is apparently not formed by the action of potassium thiocyanate on the hydrochloride of glutaminic acid in aqueous

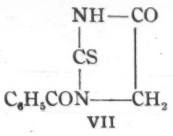
[1] J. Pharm. Chim., **30**, 145 (1909).

or alcoholic solutions. We have also applied our new method[1] of synthesizing 2-thiohydantoins from α-amino acids by heating glutaminic acid with potassium thiocyanate in acetic anhydride solution. There was no evidence of the formation of the thiohydantoin (V) under these conditions, and the results obtained indicated that this amino acid is completely deamidized by this treatment. This observation is of special interest because glycocoll and alanine[2] react smoothly, under the same conditions, forming acetyl derivatives of 2-thiohydantoin and 2-thio-4-methylhydantoin, respectively.

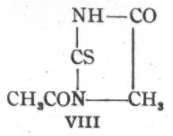
Johnson and Nicolet[3] observed that aceturic acid reacts with potassium thiocyanate, in acetic anhydride, forming the same thiohydantoin (VI) as is obtained directly from glycocoll. Hippuric acid, for example, behaved in a similar manner, giving 2-thio-3-benzoylhydantoin (VII). Alanine and acetylalanine also gave the same 2-thio-3-acetyl-4-methylhydantoin (VIII).[4] It was of special interest, therefore,



VI



VII



VIII

to examine the behavior of potassium thiocyanate, in acetic anhydride solution, towards pyrrolidonecarboxylic acid (IX). This acid may be viewed as a cyclic acylamino acid. We now find that this acid reacts smoothly with potassium thiocyanate, forming the corresponding cyclic thiohydantoin (XI). The relationship between this compound and the hydantoin of proline (X) is apparent from a comparison of their structural formulas. When this new cyclic thiohydantoin (XI) was digested with hydrochloric acid it underwent hydrolysis and was converted quantitatively into the unknown *2-thiohydantoin-4-propionic acid* (V). This thiohydantoin is

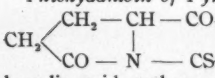
[1] Johnson and Nicolet: J. Am. Chem. Soc., **33**, 1973.
[2] Johnson: *Loc. cit.*
[3] *Loc. cit.*
[4] Johnson: *Loc. cit.*

desulphurized[1] by digestion in an aqueous solution with chloroacetic acid and converted practically quantitatively into the hitherto unknown hydantoin of glutaminic acid or *hydantoin-4-propionic acid* (XIII). This compound is of special interest because of its close relationship to glyoxalinepropionic acid[2] (XIV) and the naturally occurring amino acid histidine (XII). The study of these two interesting hydantoins will be continued.

EXPERIMENTAL PART

The Action of Potassium Thiocyanate on Pyrrolidonecarboxylic Acid

Thiohydantoin of Pyrrolidonecarboxylic Acid,



—Two grams of pyrrolidonecarboxylic acid and 1.5 grams of dry potassium thiocyanate (finely pulverized) were suspended in 9 cc. of Kahlbaum's acetic anhydride and 1 cc. of glacial acetic acid added. The mixture was then heated on the steam bath for one-half hour, when the reaction was apparently complete and a clear yellow solution was obtained. When this solution was cooled the hydantoin separated quickly in prismatic crystals. The hydantoin crystallizes from alcohol or water in long, prismatic crystals, which melt at 206° with decomposition. It is less soluble in water than in alcohol. The yield of hydantoin is good. In two experiments, in which we used 7.5 and 25.0 grams of the pyrrolidonecarboxylic acid, we obtained 7.0 and 17.0 grams, respectively, of the thiohydantoin. Analysis (Kjeldahl):

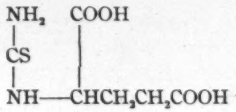
	Calculated for $C_6H_6O_2N_2S$	Found I	Found II
N	16.47	16.27	16.33

In one experiment, in which 2.0 grams of the pyrrolidonecarboxylic acid and 1.5 grams of potassium thiocyanate were used, the method of procedure was changed as follows: After heating one-half hour with acetic anhydride, as above,

[1] The question of desulphurization of thiohydantoins will be discussed in a later paper.—T. B. J.

[2] Knoop and Windaus: Hofmeister's Beiträge, 7, 144.

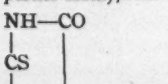
the liquid was then poured into three to four volumes of cold water and the solution concentrated on the steam bath at 100°. We obtained a viscous liquid, which deposited no crystals after standing for several hours. This syrupy material was then triturated with about 10 cc. of dilute hydrochloric acid, when a well crystallized substance finally deposited. The yield, however, was small. It was purified for analysis by crystallization from hot water and separated on cooling in large, rhombic plates, which decomposed at 205° with violent effervescence. The compound contained sulphur but was free from chlorine. A mixture of the substance with the thiohydantoin of pyrrolidonecarboxylic acid melted at 175°. A nitrogen determination agreed with the calculated value for the thiohydantoic acid derivative of glutaminic acid,



	Calculated for $C_6H_{10}O_4N_2S$	Found
N	13.79	13.60

An attempt to prepare this compound again in the same manner was unsuccessful. We obtained, as above, a syrupy residue after concentration of the solution but on triturating with hydrochloric acid the thiohydantoin of pyrrolidonecarboxylic acid separated. After crystallization from water it melted at 205°–206° and a mixture of this with the hydantoin from pyrrolidonecarboxylic acid, described above, melted at exactly the same temperature.

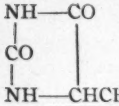
Thiohydantoin of Glutaminic Acid (2-Thiohydantoin-4-propionic Acid),



.—This compound is obtained easily by hydrolysis of the thiohydantoin of pyrrolidonecar-

boxylic acid. Two grams of this cyclic thiohydantoin were dissolved in 50 cc. of dilute hydrochloric acid and the solution evaporated to dryness. A thick, colorless syrup was obtained which crystallized immediately on cooling. The hydantoin was purified by crystallization from hot water and separated, on cooling, in rhombic plates which melted at 122° to a clear oil without effervescence. The compound is very soluble in alcohol, ether and acetic acid and insoluble in benzene. Analysis (Kjeldahl):

	Calculated for $C_5H_8O_3N_2S$	Found
N	14.9	15.1

Hydantoin of Glutaminic Acid (Hydantoin-4-propionic Acid),  .—This hydantoin can be prepared easily by desulphurization of 2-thiohydantoin-4-propionic acid with chloroacetic acid. Two grams of the thiohydantoin and 1.5 grams of chloroacetic acid were dissolved in 10 cc. of water and the solution boiled for one-half hour. It was then evaporated on the steam bath, when we obtained the hydantoin. This was purified for analysis by recrystallization from hot water and deposited, on cooling, in hexagonal, tabular prisms, which melted at 165° to a clear oil. They did not contain sulphur and the yield of purified material was 1.1 grams. Analysis (Kjeldahl):

	Calculated for $C_6H_8O_4N_2$	Found
N	16.28	16.08

Action of Chloroacetic Acid on the Thiohydantoin of Pyrrolidone-carboxylic Acid

Two grams of this cyclic thiohydantoin and 1.7 grams of chloroacetic acid were dissolved in water and boiled for about 30 minutes. The solution was then evaporated at 100°, when a viscous liquid was obtained which finally deposited crystalline material on standing. This was separated by

suction filtration and then purified by crystallization from hot water. It separated in prismatic crystals which melted at 165°, and was identified as the hydantoin of glutaminic acid. The yield, however, was much smaller than when the thiohydantoin of glutaminic acid was desulphurized with chloroacetic acid.

The Action of Potassium Thiocyanate on Glutaminic Acid

In Alcoholic Solution.—In this experiment, 4 grams of the hydrochloride of glutaminic acid and two molecular proportions of finely pulverized, dry potassium thiocyanate were dissolved in 100 cc. of absolute alcohol and digested on the steam bath for exactly one hour. The solution took on a red color, potassium chloride deposited, and within 15 minutes the solution became almost colorless. After cooling, the potassium chloride was filtered off and the filtrate evaporated to remove the alcohol. We obtained an oil which partially solidified on cooling. This material was extremely soluble in cold water. An excess of dilute hydrochloric acid was then added, the substance dissolved and the solution evaporated again to dryness. This time a semisolid residue was obtained. The product was then extracted with absolute alcohol, when we obtained 2.5 grams of crystalline, insoluble material, which proved to be chiefly ammonium chloride and contained no organic material. The alcohol extract, on evaporating, left behind a viscous oil, which we then triturated with ether to remove any 2-thiohydantoin-4-propionic acid. None was obtained. This residue, which was insoluble in ether, dissolved immediately in cold water, except a small amount of sulphur present, and the solution gave a strong test for ammonia when treated with some sodium hydroxide solution. No crystalline material deposited on standing.

In Acetic Anhydride Solution.—Although we tried several experiments with this solvent, we did not succeed in isolating, in any case, a crystalline product except ammonium chloride. Barium thiocyanate was also used instead of potassium thiocyanate, but with no greater success. In order, therefore,

to obtain some explanation for these negative results, we performed the following experiment:

Two grams of glutaminic acid and 1.5 grams of potassium thiocyanate (dry and finely pulverized) were suspended in a mixture of 9 cc. of acetic anhydride and 1 cc. of glacial acetic acid. On heating at 100° the thiocyanate dissolved and a clear yellow solution was obtained. After heating 30 minutes and cooling, the solution was then diluted with hydrochloric acid and finally evaporated to dryness. The residue was then dissolved in water, the solution made alkaline with sodium hydroxide and distilled from a Kjeldahl flask. The ammonia evolved was conducted into a hydrochloric acid solution and this then evaporated to dryness. We obtained in this manner 1.2 grams of pure ammonium chloride, while the theoretical amount, corresponding to all the nitrogen available in potassium thiocyanate and the glutaminic acid, is 1.5 grams.

NEW HAVEN, CONN.
February 2, 1912

NOTES

The Density of Niton ("Radium Emanation") and the Disintegration Theory[1]

According to the disintegration theory of radioactive change a definite number of atoms of radium break up per second, each evolving an α particle which ultimately becomes a helium atom, leaving behind lighter molecules which form the gas known as "radium emanation," or niton. The identity of the α particle after it has lost its electric charge with the helium atom has been convincingly proved by Rutherford and Geiger; and measurements of the volume of helium evolved from niton by Ramsay and Soddy, and from radium in equilibrium with its disintegration products by Dewar, render it exceedingly probable that in each successive change from radium to radium D only one α particle is expelled per atom.

If, then, the view is held that the radium atom on disintegration to niton splits up into two parts only, one of which is the α particle, then the atomic weight of the resulting niton is $226.4 - 4 = 222.4$. On the other hand, it may be sup-

[1] A paper read before the Royal Society and printed in the P. Roy. Soc., **81, A,** 536; Chem. News, **103,** 85, 99.

posed that the disintegrating radium atom splits up into three or more parts; helium, and two other bodies of higher atomic weight, if three parts. On account of its greater mass, the heavier particle might be expelled below the critical velocity necessary for the formation of ions in the air, and might itself be nonradioactive; if this were the case, its presence in a solid state would almost certainly escape detection. There is no direct evidence against such a supposition, for the atomic weights of none of the products of the disintegration of radium have been determined. Experiment alone can settle this question of the true atomic weight of niton; but on account of the exceedingly small volume of this gas obtainable from a relatively large weight of radium, the experiment is by no means easy.

A number of investigators have sought to obtain the atomic or molecular weight by comparing the rates of diffusion of "emanation" and air or nitrogen:

	Found
Pierre Curie and Danne[1]	176
Bumstead and Wheeler[2]	180
Rutherford and Miss Brooks[3]	176
Makower[4]	100
Chaumont[5]	70–100

Perkins compared the rate of diffusion with that of mercury vapor, also a monatomic gas, and found 235.[6]

Lastly, Debierne made use of Bunsen's method of causing the gas to issue through a minute perforation in a diaphragm of platinum, and as the result of a very concordant set of experiments, obtained the number 220 for the molecular weight.[7]

But none of these methods, however ingenious, can be accepted as conclusive, for the conditions are so different from those usually obtaining in ordinary work that no certain inference can be drawn.

In 1909 we attempted the solution of this problem in another way.[8] We found it possible to determine the critical and boiling points of niton with less than one-tenth of a cubic mm. of gas. Assuming it to belong to the inactive series of gases, we plotted the critical and boiling points of argon, krypton and xenon against their atomic weights, and found these points to lie almost exactly on a slightly curved line.

[1] Compt. rend., **137**, 1314 (1903).
[2] Am. J. Sci., **1904**, 97.
[3] Trans. Roy. Soc., Canada, **1901**.
[4] Phil. Mag., **1908**.
[5] Le Radium, **6**, 106 (1909).
[6] Am. J. Sci., **1908**, 461.
[7] Compt. rend., **150**, 1740 (1910).
[8] J. Chem. Soc., **95**, 1073.

Extrapolation showed that for the emanation to lie either on the line connecting the boiling points or the critical points, it must possess an atomic weight approximating to 176. It was quite impossible to bring the value 222.4 anywhere near the extrapolated curves; but it must be observed that, as the curvature is slight, a small error in the constants of argon, krypton or xenon might alter the curvature in the reverse direction, and so make more probable the higher atomic weight. We realized at the time that the results could not be accepted as certain, and that the only criterion must be the determination of the density of the gas. It is, however, remarkable that all the determinations quoted, with the exception of Makower's and Chaumont's, point to an atomic weight either of 176 or of 222; these are the tabular atomic weights of the immediate follower of xenon in the Periodic Table, on the one hand, and of the next member on the other. The members of the series are:

Helium	Neon	Argon	Krypton	Xenon	I	II
4	20	40	83	130	176	222

To determine the density of a gas, four separate measurements are essential—the volume, the temperature, the pressure and the weight of the gas. In the present case, however, the problem was simpler, for the volume of niton at normal temperature and pressure accumulating in a given time from a known weight of radium is a constant and invariable quantity, and has been repeatedly measured. In 1908 Rutherford found this volume to be 0.61 cubic mm. per gram of radium; Debierne, in 1909, obtained the value 0.58 cubic mm., and these results were confirmed shortly afterwards by our own work,[1] which gave 0.601 cubic mm. Rutherford has been able to calculate this constant from the result of his beautiful experiment in which he actually counted the number of α particles emitted from a known weight of radium, and the value found was 0.585 cubic mm. It may therefore be taken as certain that the error in this constant does not exceed 5 per cent. For our experiments this figure is unessential, since the actual volume of emanation from the total radium at our disposal had been measured.

The problem which we have attacked is the determination of the weight of emanation evolved in a given time from our total quantity of radium. The radium bromide solution from which the niton for these experiments was drawn was contained in three bulbs sealed on to a Töpler pump. The

[1] *Loc. cit.*, p. 1082.

maximum measured quantity of emanation which can be extracted with the pump from the solutions in the bulbs is 0.127 cubic mm. By collecting the gas every eight days, the yield was only 76 per cent. of this quantity, so that the total volume obtainable for weighing scarcely exceeded 0.1 cubic mm. The weight of this volume, on the assumption that the atomic weight is 222, is less than $^1/_{1400}$ mg. It is therefore evident that in order to weigh this minute quantity of gas with sufficient exactness, a balance turning with a load not greater than $^1/_{100000}$ mg. was a necessity. This seems an almost inconceivably small weight to attempt to measure, when one considers that the limit of sensibility of a delicate assay balance is about $^1/_{200}$ mg., and that even the Nernst balance will hardly turn with a load smaller than $^1/_{2000}$ mg. (As we shall have to deal with very small weights, it is advisable to adopt a new unit; this is conveniently the millionth of a mg. The abbreviation here used for this is μmg.)

The successful construction of a balance capable of weighing these very minute quantities has been accomplished by Dr. B. D. Steele and Mr. Grant, of the University of Melbourne; thanks to their skill and ingenuity, they have constructed an instrument 100 times more sensitive than the Nernst microbalance. Steele and Grant have published an account of their balance,[1] and they have shown that a sensibility of $^1/_{250000}$ mg. could be attained. After several trials we have been successful in constructing a similar instrument and in determining the density of the radium emanation with its help. It is only fair to state, however, that Dr. Brill, working in the laboratory of University College, improved the Nernst balance, so that it turned with $^1/_{10000}$ mg. The subject was followed up later by Dr. Gwyer, also at University College, who introduced the hydrostatic method of determining small weights, the buoyancy of a small bulb containing a known weight of air being altered by the adjustment of the pressure in the balance case, constructed so that a vacuum could be made. We then corresponded with Dr. Steele, who was so obliging as to inform us of the principles and construction of his balance, then in an experimental stage.

The paper published by Steele and Grant renders a minute description of our balance unnecessary; but our balances (for several were constructed) differ in some small respects from theirs. The beam, for example, was made by placing thin silica rods in grooves carefully ruled on a smooth plane block of graphite, and then fusing the contiguous ends together in

[1] P. Roy. Soc., **83**, A, 580 (1909).

an oxygen-coal gas flame; in this way, a symmetrical beam, lying on a plane surface, was secured. If this condition is not fulfilled, the beam is apt to be deformed by small stresses set up in the quartz at the points of junction, as found by Steele and Grant. It is also necessary that the knife edge shall be at right angles to the beam in two planes. This was managed by sealing the knife edge on to the beam with a long guiding rod of silica attached to it, so that adjustment to a right angle is not difficult by trial and error; this guiding rod, when fused off, left a stem of a few mm. in length, to which the platinized silica mirror was fused. By this device the mirror revolved without displacement when the balance was deflected. Another improvement was the direct sealing of a fine quartz fiber to the end of the beam, whereby a much freer suspension was attained. Again, while Steele and Grant weighed by displacement of the zero, our weighings were made by a null method, whereby the alteration of pressure brings the spot of light to its original position. In this way, any possible variation in the sensibility of the beam with its deflection from horizontality is avoided. To eliminate as far as possible temperature changes and also vibration, the balance is mounted on a stone pillar in a cellar, and the brass case stands inside a large box of bright tin-plate. The mirror is illuminated by a beam of light from a Nernst lamp, which reflects on to a mm. scale about 3 meters away. The light is allowed to impinge on the mirror only when a reading is taken.

The small counterpoise quartz bulb, which contains a known weight of air, serves instead of a set of weights. When the air pressure in the balance case is the same as that in the bulb the apparent weight of the air which it contains is nil. That is to say, the real weight of the air in the bulb is exactly counterpoised by the buoyancy of the air outside. In a vacuum the sealed-up air exerts its full weight, and at any intermediate pressure the arm of the beam carrying the bulb is loaded with a known fraction of this weight. The counterpoise bulb of the balance used by us has a capacity of 22.2 cubic mm., and the air which it contains weighs 0.027 mg., or 27,000 μmg. (millionth mg.). A pressure change of 0.1 mm. can be easily read by a cathetometer, so that any object lighter than 27,000 μmg. can be weighed with an accuracy of 3.55 μmg.

By reading the pressure more exactly, say, to 0.01 mm., the limit of accuracy could have been increased to one-tenth of the figure above, provided, of course, that the sensibility of the balance is great enough; to obtain this maximum degree of sensibility two important conditions have to be fulfilled.

The center of gravity of the beam must be most carefully adjusted, and the knife edge must be perfectly straight and regular, even when viewed through a microscope with a half-inch objective. The final adjustment of the center of gravity is made by volatilizing away from the top of the center rod, round which the beam is built, minute quantities of quartz in the oxy-coal gas blowpipe; this is a comparatively simple process. The making of the knife edge gave a good deal of trouble, but in the end this difficulty was overcome. The edge itself is about 0.3 or 0.4 of a mm. long, and is ground in the form of a right-angled prism on the end of the quartz rod, which is subsequently fused on to the beam. The grinding and polishing of the edge, which is a very delicate operation, was carried out for us by Messrs. Hilger and Co.

Our present balance is sensitive to about 2 μmg.; its zero remains perfectly constant for days together. When the counterpoise bulb is removed, the zero of the balance is not altered by large changes of pressure within the case.

The standard of weight, which is, of course, the weight of the air in the counterpoise bulb, has been verified in the following way: A long measured length of very fine aluminium wire was weighed as accurately as possible on an assay balance. A small portion of this wire, about 2 mm. in length, was cut from the longer length in such a way that the cross sections were as nearly as possible circular; it was then measured under a reading microscope, and its weight was determined in terms of the counterpoise bulb on the microbalance. The weight so determined agreed within 1 per cent. with the weight calculated, on the assumption that the wire was uniform and that the weight of the small piece was directly proportional to its length.

For the measurement of the density of very small quantities of niton or of other gases, the following procedure was adopted: The gas, of a volume of the order of 0.1 cubic mm., was forced by means of mercury into a fine capillary tube of about 1 mm. external and 0.2 mm. internal diameter, which was sealed on to the apparatus for purifying the gas. The upper end of this tube was drawn out into a finer very thin-walled tube, the extreme point of which was sealed. When necessary, the volume of the gas was measured at various pressures in the capillary tube, carefully calibrated for this purpose. After measurement, the tip of the tube was surrounded for some time with liquid air, in order to condense the gas; the volume of the gas was then considerably increased, so that any hydrogen still present should expand, and only a minute

trace could remain at the top of the tube; the tube was then sealed at a distance of about 20 mm. below the tip, by the aid of a pin-point gas flame. After most carefully cleaning and drying the small tube, it was lifted with platinum-tipped forceps, the tips of which had just been heated to redness, and placed in a little tightly-fitting bucket, or external tube, of silica, suspended from one arm of the balance by quartz fiber; this pointed end of the density tube was downwards, and the lower end of the bucket was slightly curved. A quartz counterweight suspended to the same arm of the balance was then adjusted, by fusing on or by volatilizing off small pieces of silica, so that the beam was in balance at a pressure in the neighborhood of 50 mm. After an hour or more the pressure in the case was exactly measured, and the position of the spot of light on the scale was noted. The bucket and tube were then removed with the platinum-tipped forceps; and while it was held vertical inside a wider tube, the density tube was pressed down with a glass rod, cup-shaped at the end; the drawn-out point of the density tube broke, but no splinters of glass could escape, for they were all retained in the bucket of silica. The bucket and its tube were then replaced on the balance, and the air was exhausted; air was again admitted, and a second exhaustion was made; in this way the gas was removed from the interior of the density tube, and replaced by air. The pressure was then adjusted to bring the zero point back again to its original position. With practice, the whole operation could be carried out in less than five minutes; this reduced the chance of error from the condensation of moisture on the glass and the settling of dust particles.

Before experimenting with the precious niton, the method was tested with the less valuable xenon. Before freezing the gas its volume was measured; it amounted, at 0° and 760 mm., to 0.0977 cubic mm. It was then frozen, and the density tube was sealed off and placed in its bucket on the balance; after breaking the tip, the pressure change was 17.1 mm. (70–52.9); the temperature change was too small to affect the result; this pressure change corresponds to an apparent loss of weight of 608 μmg. But this number does not represent the real weight of the xenon, for in the second weighing the tube is full of air, and therefore to the observed weight the weight of the air filling the tube at the temperature and pressure of the second weighing has to be added. The volume of the tube being known (for its length was measured), the weight of air under the conditions of weighing (52.9 mm.

and 16°) proves to be 46 μmg.; hence the total weight is 654 μmg. A further correction has next to be applied to allow for the difference in buoyancy of the glass of the weighing tube in the two weighings. This correction could, of course, be calculated, provided one knew the weight of the tube, the density of the quartz of the silica counterpoise on the end of the beam opposite to the objects to be weighed, and the density of the sample of glass forming the weighing tube. It was found, however, to be more accurate and convenient to determine directly on the balance the magnitude of this correction for each experiment. For this purpose the counterpoise bulb containing air was replaced by a piece of quartz of almost exactly the same weight, and under the new conditions the variation of the zero point on the balance for a given change of pressure was determined. Knowing the weight corresponding to each scale-division displacement of the zero point, the variation in buoyancy of the open glass tube between the two weighings was easily and accurately determined. In general, this correction is a somewhat large one, and amounts in this case to no less than one-seventh of the total weight of the gas. The reason for this is the large difference in weight between the density tube and the contained gas. The density tube, as a rule, weighed about 30 mg., and the contained gas about $^1/_{2000}$ mg.; hence the weight of gas is to that of the vessel as 1 to 60,000, whereas, under ordinary conditions, when weighing 200 cc. of gas, the ratio is about 1 to 600.

In this experiment, the correction for the buoyancy of the glass proved to be 91 μmg.; but there is still a correction to be applied, for there is a change of buoyancy due to the volume occupied by the gas itself. As the volume of the tube was known, this could be calculated with greater accuracy than it could be determined by experiment. In this case, the xenon occupied 0.536 cubic mm., and the difference in buoyancy of the air between the pressures 70 and 52.9 mm. (17.1 mm.) is $17.1 \times 0.536 \times 1.29/760 \times 1000 = 15$ μmg. Had the sealed tube been weighed at the lower instead of the higher pressure (at 52.9 instead of 70 mm.), it would have weighed more, hence this correction is positive. The true weight of the xenon is therefore $654 - 91 + 15 = 578$ μmg. The calculated weight of 0.0977 cubic mm. of xenon is 577 μmg. The exact agreement is doubtless a coincidence.

With niton, two sources of error made their appearance; in the first place, the density tube became strongly electrified, and attracted dust particles and adsorbed air, and in the second, the tube was always at a higher temperature than the

surrounding atmosphere during weighing,[1] and convection currents were liable to be set up in the air surrounding one limb of the balance. The first of these effects could not be entirely eliminated, but it was considerably reduced as regards dust by filtering the air through a long column of tightly packed cotton wool before allowing it to enter the balance case. In addition, the tube, after suspension from the beam of the balance, was, as a rule, gently heated by passing a non-luminous pin-pointed gas flame quickly over its surface, thus burning off most of the attracted particles of dust. The same expedient was also adopted, before the second weighing, after the tube had been broken. Blank experiments showed that this procedure did not alter the weight of the tube in the slightest degree, provided it was perfectly clean; when dust particles were present, however, there was always a small loss of weight.

The effect of convection currents was reduced as much as possible by weighing at a low pressure; in our five experiments, the final pressure varied from 87 to 13 mm.; and the concordance of the results precludes the possibility of any serious error from this source. It may also be noted that the density tube, after removal of the niton and during the second weighing, contained approximately the equilibrium amount of radium A, B and C, the heating effect of which is a large fraction of the total heating effect of the emanation in equilibrium with its quick-change products; hence any error in the first weighing was partially compensated by a similar error in the second weighing. Finally, we would point out that convection currents, on account of the position and shape of the tube, have very little influence on the balance, and their presence should have been revealed by the oscillations of the beam and the position of the zero point. No irregularity, however, was noticed, and we believe that this source of error produced only negligibly small effects.

Before proceeding to cite the experimental results, we have still to explain how the exact volume of niton weighed was ascertained. Taking as a basis our previous measurements, which proved the equilibrium amount of niton yielded by the total amount of radium at our disposal to be 0.127 cubic mm. at normal temperature and pressure, we had to determine what fraction of this amount was actually present in our weighing tube. This was conveniently done by measurement of the γ ray activity by help of a small aluminium electroscope. The procedure was as follows:

[1] See Ramsay: J. Chem. Soc., **91**, 931 (1907).

The emanation was drawn off from the radium bulbs at definite intervals of time, usually eight or nine days. After explosion of the mixed oxygen and hydrogen gases it was allowed to stand for several hours, so that the quick-change products should accumulate; and its γ ray activity was measured in the usual way. It was next introduced into the density tube, and frozen there, as described for xenon, and the hydrogen was removed by pumping; about 10 per cent. of the niton was pumped off with the hydrogen, for the niton has some vapor pressure at —195°. The γ ray activity of the gas removed was compared with that in the sealed-off density tube, after a suitable interval of time. Other measurements were made to determine the quantity remaining in the purifying apparatus; but in most cases this was negligible, and, as a rule, the radioactivity of the pumped-off gas, plus the radioactivity of the gas in the weighing tube, were together equal, after corrections for the decay had been made, to the initial total radioactivity of the gas before it had been purified. It was found, however, that some niton had entered the walls of the weighing tube; this fraction was estimated by determining the radioactivity of the empty tube, immediately after it had been weighed. Obviously, this emanation had not been removed by the pump. In the table which follows, this amount appears in the column "volume left in tube;" it has been subtracted from the total volume.

The operation of drawing and purifying the emanation, measuring its radioactivity, counterpoising and weighing the density bulb, and measuring the radioactivity of the amount pumped off, as well as that in the weighing tube, required a long day, so that the density tube could not be broken until twenty-four hours after the niton was drawn; the actual volume of niton present at the moment of fracture, however, was easily calculated from the known rate of decay.

As the quick-change products, A, B, and C are short-lived and change rapidly into D, and as D is a solid, it remains in the density bulb, and is not weighed, but the helium resulting from the change of niton into A, A into B, and C into D, escapes for the most part along with the niton; its weight must be calculated, and that of the escaping gas diminished by this amount, in order to arrive at the true weight of the niton.

Five experiments were made in order to determine the total loss of weight on opening the density tube, and a sixth to obtain an estimate of the weight of the helium produced by the disintegration of the niton as far as radium D. For this purpose a density tube was filled as described in the middle of the

month of July, 1919; it remained counterpoised on the balance until October, when the conversion into D was practically complete. As the half-life period of D is about fourteen years, it is unnecessary to consider any further change. At the end of October the point of the density tube was broken as usual, and the tube was again weighed, the loss in weight being due to the helium produced.

We must here chronicle the fact that during the three months in which the tube hung on the balance a continuous gain in weight was noticed, rapid at first, but attaining an end-point; this amounted to 670 μmg. On heating the tube, 1280 μmg. were lost. The tube had not been heated before it was originally suspended on the balance; the gain was probably due to condensation of air on the electrified surface, and possibly, but improbably, to the deposition of dust. This gain of weight on standing is, however, not confined to electrified surfaces; a gold capsule, heated to redness before suspension, gained considerably in weight for two days. The density tube was heated, and resuspended on the balance, and for three hours there was no alteration of weight. It was then broken and immediately placed on the balance, and weighed within five minutes, during which it might be expected that no change would occur; the loss of weight was 15 μmg. The volume of the density tube was 0.196 cubic mm.; the weight of air filling it at 37.7 mm. pressure and 18°.5 C. was 12 μmg.; hence the total weight of helium was 27 μmg.; no correction for glass displacement of air was necessary, for the pressure did not vary during the readings.

The calculated weight of helium obtainable from 0.072 cubic mm. of niton, the amount present in the tube, on the assumption that each atom (or molecule) of niton loses three α particles on disintegrating to radium D, should have been 38 μmg.; of this, only about three-quarters had been removed by the pump. It was necessary to seek for the remainder, which, we believed, had entered the glass of the weighing tube.

Before removing it, however, we thought it worth while to attempt to dissolve the deposit of radium D from the walls of the weighing tube, and to estimate its amount by loss. The closed end of the weighing tube was cut off, and the rest of the tube placed in the bucket along with it, and weighed. The tube itself was then washed out with a mixture of two drops of nitric acid, previously purified by distillation from a silica bulb, and one of water; the solution was preserved. The tube was then washed with water and dried by aspirating

through it a current of dry air; it was then replaced in the bucket and reweighed. The loss was 831 μmg. Supposing that the emanation, the calculated weight of which, assuming it to have the atomic weight 222.4, was 713 μmg., had lost three α particles, the weight should have been 674 μmg. The difference, as we have proved by a subsequent experiment on the solubility of glass in dilute nitric acid, is due to the removal of sodium and calcium as nitrates. This must have amounted in the case given to 831–674 = 157 μmg. We identified under the microscope crystals of sodium nitrate.

It is obvious that no importance can be attached to the latter half of this experiment, except inasmuch as it shows a loss of weight of the order required.

The weighing tube still contained presumably occluded helium. It was placed in a silica tube, surrounded by a thicker-walled tube, also of silica, and it was connected with a Töpler pump, and with an inverted siphon for introducing oxygen. The apparatus was freed from air, and washed out several times with oxygen, so as to avoid introducing helium or neon from the air. About one-third of a cc. of oxygen was then admitted, and the silica tube was heated in a blowpipe flame until the glass weighing tube had completely fused; small bubbles were evolved. The oxygen, together with the gas evolved from the tube, was pumped off and introduced into an apparatus consisting of a calibrated capillary tube in communication with a minute bulb containing charcoal cooled with liquid air. After some hours the oxygen was completely absorbed by the charcoal, and the residual gas was measured. The correction for the unmeasured gas still remaining in the charcoal bulb was found to be 4 per cent. The volume was 0.042 cubic mm. at 0° and 760 mm. pressure, and its weight was therefore 8 μmg. The sum of the helium actually weighed (27 μmg.) plus that measured (8 μmg.) gives a total of 35 μmg., differing from the calculated amount (38 μmg.) by only 3 μmg. That the gas measured was pure helium was proved by surrounding the upper part of the capillary tube with tinfoil, and passing a discharge from a coil through it. The full spectrum of pure helium was seen, and no other lines.

The result has astonished us, as, perhaps, it may astonish our readers, but the conditions under which the last weighing was made were particularly favorable, since the tube was practically nonradioactive.

This experiment taught us that about one-quarter of the helium produced by the disintegration of the emanation and

Table of Results

No. of expt.	Time of accumulation. Days	Total volume of niton. Cu. mm.	Volume pumped off Cu. mm.	Decay of niton. Cu. mm.	Volume left in tube. Cu. mm.	Volume weighed. Cu. mm.	Apparent weight. Micromg.	Weight of air replacing niton. Micromg.	Correction for diplacement due to glass and air. Micromg.	Correction for weight of helium produced from niton. Micromg.	True weight of niton Micromg.	Atomic weight of niton.
1	8	0.0969	0.0052	0.0182	0.0007	0.0728	721	+ 31	—29 + 24	— 8	739	227
2	9	0.1017	0.0188	0.0163	0.0100	0.0566	477	+103	—16 + 15	— 7	572	226
3	9	0.1017	0.0135	0.0253	0.0039	0.0590	577	+ 37	—22 + 9	—10	591	225
4	8	0.0969	0.0119	0.0157	0.0016	0.0677	673	+ 10	—26 + 12	— 6	663	220
5	8	0.0969	0.0082	0.0152	0.0005	0.0730	704	+ 29	—33 + 16	— 6	710	218
											Mean,	223

A complete reproduction of Experiment 5 may be given, to show how all the requisite data are obtained and utilized.

Volume of niton accumulated in eight days = equilibrium quantity × fraction surviving

0.127 × 0.763 ..... 0.0969 cu. mm.

γ ray activity of this sample, divisions per hour ... 3996 divisions

γ ray activity of fraction pumped off ..... 335 "

Hence amount pumped off ..... 0.0082 cu. mm.

Amount of niton in weighing tube = 0.0969—0.0082 ..... 0.0887 "

The weighing tube was then counterpoised on the balance.

Pressure in balance case ..... 54.4 mm.

Zero on scale of beam of light reflected from mirror ..... 155 "

Twenty-five hours after drawing, the weighing tube was broken. The gas pumped out, however, was not the original 0.0887 cu. mm., but that volume multiplied by the decay factor for twenty-five hours, 0.828, viz. ..... 0.07347 cu. mm.

Pressure in balance case after breaking the density tube ..... 34.7 mm.

Pressure change = 54.4—34.7 ..... 19.7 "

Zero on scale after breaking ..... 154 "

Difference of zero = 155 — 154 = 1 mm. But from measurement, 10 mm. pressure = 77 scale divisions; hence 1 division = 10/77 = 0.13 "

This must be added to the pressure — 19.7 + 0.13 = ... 19.83 "

The counterpoise bulb contained 0.0270 mg., or 27,000 μmg. of air. Its buoyancy was altered (19.83/760) × 27,000 = ... 703.8 μmg.

But air entered the tube when it was broken; the volume of the density tube, ascertained by previous calibration, was 0.522 cu. mm. Weight of this air at 34.7 mm. and 17° C. = 0.522 × 1290 × 35/760 × 273/290 = ... 29.2 μmg.

The sum of these quantities, 703.8 and 29.2 ..... 733 "

But the pressure was changed by 19.8 mm.; this alters the weight of the density bulb by the weight of air corresponding to the difference in volume between the glass density bulb and a silica one; as already described, this quantity was determined directly by replacing the air bulb by a solid counterpoise of silica, and using the density bulb as a measure of buoyancy. For 19.8 mm. the "glass displacement" is equivalent to —32.8 μmg. A further correction has to be made, viz., the change of buoyancy due to the volume occupied by the gas itself. The volume of the density tube was 0.522 cu. mm.; the change of pressure was 19.8 mm.; hence the weight of this air for 19.8 mm. change = 0.522 × 1290 × 19.8/760 × 273/290 = 16 μmg. This is a positive correction; the weight, 733 μmg., must be diminished by the difference between 32.8 and 16, say, 17 μmg. The remainder is 716 μmg.

The last correction to make is the subtraction of the weight of the helium produced by the decay of the emanation during its stay in the weighing tube. Now,

22,400 cu. mm. niton weighs, say, 222.5 mg., and

0.0224 cu. mm. niton weighs, say, 222.5 μmg.

Each atom of niton gives three atoms of helium; hence, helium from 0.0224 cu. mm. niton weighs 12 μmg. The volume of emanation decayed in the weighing tube is 0.0887 cu. mm. — 0.0735 cu. mm. = 0.0152 cu. mm., and the weight of three times that volume of helium is 8 μmg. One-quarter of this has entered the glass and has not escaped, hence the helium removed weighed 6 μmg. That number deducted from 716 leaves 710 μmg. as the weight of the niton.

To return for a moment to its volume. The amount of niton in the weighing tube was 0.07347 cu. mm. at the moment of pumping out. But some niton had penetrated its walls, and was not removed by the pump. That amount was estimated by comparing the γ radioactivity of the weighing tube after it had been weighed "empty" with that of the gas pumped off, which had, of course, diminished in radioactivity; this diminution corresponded with the time which had elapsed since the last reading, and was measured to verify the constancy of the electroscope. The radioactivity of the residue left in the weighing tube was, after correction for natural leak, 17 divisions per hour. The original radioactivity of the niton in the weighing tube was 3996 — 353 = 3643 divisions per hour; its volume in the weighing tube when decay commenced was 0.0887 cu. mm.; hence the "volume" left in the tube by the retention of niton in the walls was (17 × 0.0887)/3643 = 0.0005 cu. mm. This, subtracted from 0.07347 cu. mm., the volume of the niton in the tube at the moment of pumpinng out, leaves 0.0730 cu. mm. as the volume actually weighed.

All the data are now complete; 0.0730 cu. mm. of niton at 0° and 760 mm. pressure weighed 710 μmg. A liter weighs 9.727 grams; a liter of oxygen weighs 1.429 grams; and the molecular weight of niton is therefore 218.

its products enters the walls of the weighing tube, and is not removed by the pump; we have now all the data for calculating the density of niton. The results are given in the accompanying table.

The nomenclature of Rutherford and Soddy, which has attained the provisional assent of the Brussels Congress, is advantageous as showing the relationship between the degradation products of the various radioactive elements, but obscures any chemical relationship between the elements themselves. Were it consistently carried out, radium, which undoubtedly belongs to the group of alkaline-earth metals, would have to be named after uranium, a metal with no affinities with that group. The "emanation of radium" is a cumbrous name, and gives no indication of its position in the Periodic Table, a position which may now be taken as certain. To show its relation to gases of the argon series, it should receive a similar name; and the spectrum, the freezing point, the boiling point, the critical point, the density of the liquid, and the density of the gas, the last establishing, without doubt, the atomic weight of the element, having been determined in this laboratory, it only remains to give it a name. The name niton, Nt, which has been used in this paper, is suggested as sufficiently distinctive.

The research, of which the foregoing is an account, yields a further proof, if such were necessary, of the beautiful theory of the disintegration of the radioactive elements originally advanced by Rutherford and Soddy in 1902. The determination of the density of a gas, even with approximate exactness, has always been regarded as establishing its molecular weight, the accurate values of which have been derived from other considerations. In the present case, these considerations are the result of the disintegration theory. Determinations by Madame Curie and by Thorpe of the atomic weight of radium show beyond all doubt that it differs little from 226.4. That four atoms of helium separate from one atom of radium is rendered almost certain from the work of Dewar, and from experiments by Rutherford, and by Ramsay and Soddy. That three atoms of helium are lost by niton on decay has been shown in the preceding pages. It follows that one helium atom must escape when radium changes into its emanation; hence the true atomic weight of the emanation must be 222.4. This number hardly differs from the mean of the atomic weight determinations given in this paper; and the disintegration theory receives a further confirmation.

R. Whytlaw Gray and William Ramsay.

University College
London

OBITUARY

HEINRICH VON BRUNCK

Probably the most severe loss ever suffered by the German chemical industries was in the death of Heinrich von Brunck, which occurred on December 4, 1911. Brunck was born March 26, 1847, at Winterborn, in the Bavarian Palatinate. The interest aroused in that agricultural district by Liebig's teachings turned young Brunck's attention to chemistry, and he studied successively at the Zurich Polytechnic, then under the direction of P. Bolley, at the University of Ghent, where Kekulé was teaching, and at Tübingen under Strecker. At the latter university he obtained his doctor's degree in 1867. Shortly afterwards he secured a position as chemist in the factory of E. de Haen in Hannover, but two years later entered the employ of the Badische Anilin- und Soda-Fabrik, with which he remained connected until the day of his death. He was first entrusted with the direction of the manufacture of fuchsin and chloral hydrate. On the breaking out of the Franco-Prussian war he obeyed his country's call to arms, but when hostilities ceased he returned to Ludwigshafen. After two years at Duisberg with the factory of G. Siegle, a branch of the Badische Fabrik, where he was engaged in the purification of English crude anthracene and the preparation of chromates, he again returned to Ludwigshafen to direct, in conjunction with his friend and countryman, Carl Glaser, the manufacture of alizarin, to which he devoted himself almost exclusively until 1884. His greatest achievement, during this period, was the preparation of alizarin blue and its bisulphite compound and the application of these substances to wool dyeing. In 1879 he had obtained representation in the administration of the corporation and in 1884 was made director. With Glaser and Caro he undertook the management of the establishment, the departments of inorganic products and chlorine derivatives, alizarin and methylene blue coming under his especial direction. It was under his management that the manufacture of phthalic acid from naphthalene, the preparation of chromates, the direct oxidation of toluene to benzoic acid and benzaldehyde, the contact process for the manufacture of sulphuric acid and the synthetic production of indigo were developed. In 1907 he resigned from the board of directors but remained connected with the establishment in an advisory capacity. His retirement in no way

decreased his interest in the affairs of the concern. During these later years the problem of the utilization of atmospheric nitrogen, which is being so thoroughly investigated by the Badische Anilin- und Soda-Fabrik, chiefly engaged his attention.

A man of such abilities naturally had honors heaped upon him. He was a member of innumerable scientific societies, in many of which he had been elected to office, served on various government commissions, had been awarded numerous Prussian and Bavarian orders, the cross of the French Legion of Honor, the Turkish Order of Medjidie, and in 1905 was granted a patent of nobility. C. A. R.

REVIEWS

JAHRBUCH DER CHEMIE. Bericht über die wichtigsten Fortschritte der reinen und angewandten Chemie. Unter Mitwirkung von H. BECKURTS, Braunschweig; M. DELBRÜCK, Berlin; J. M. EDER, Wien; P. FRIEDLÄNDER, Darmstadt; C. HAEUSSERMANN, Ludwigsburg; A. HERZFELD, Berlin; EDV. HJELT, Helsingfors; K. A. HOFFMAN, Berlin; G. KEPPELER, Hannover; E. KNECHT, Manchester; J. LEWKOWITSCH, London; A. MORGEN, Hohenheim; B. NEUMANN, Darmstadt; M. NIERENSTEIN, Bristol; P. RONA, Berlin; O. SACKUR, Breslau; herausgegeben von RICHARD MEYER, Braunschweig. XX Jahrgang. 1910. Braunschweig: Druck and Verlag von Friedrich Vieweg & Sohn. 1911. pp. 568.

The Jahrbuch is so favorably known that it is only necessary to call attention to the appearance of the volume for 1910. This happens to be the twentieth volume. The editor says that the general plan and arrangement of the material have remained practically unchanged. In the first volume there were fourteen chapters, which were prepared by twelve coworkers. The number of chapters has now increased to seventeen and the number of co-workers to twenty. Nevertheless, the size of the Jahrbuch has not been increased. Professor Aschan, who has hitherto prepared the chapter on organic chemistry, has been obliged to withdraw, and Professor Edv. Hjelt, of Helsingfors, has taken his place. So also P. Rona, of Berlin, has taken the place of Dr. Spiro, who has hitherto prepared the section on physiological chemistry. It is fair to assume that this volume will prove as helpful as its predecessors. It is practically indispensable to the chemist, whatever line of work he may be following. It is more than a book of reference; it is well adapted for reading purposes. Any chemist will find in it much that is suggestive and profitable.

I. R.

FAMOUS CHEMISTS. E. ROBERTS, B.Sc. (London). The MacMillan Company. 1911. pp. 247. Price, $0.80.

Quoting from the preface: "The object of this little book is to give an account of the chief work of the most famous chemists, and to indicate briefly the part played by each in the development of the science." The chemists who are the subjects of the twenty-six brief chapters are Stahl, Boyle, Black, Cavendish, Priestley, Scheele, Lavoisier, Berthollet, Dalton, Davy, Gay-Lussac, Berzelius, Faraday, Dumas, Wöhler, Liebig, Graham, Bunsen, Hofmann, Pasteur, Williamson, Frankland, Kekulé, Mendeléeff, Perkin, and Meyer. In consequence of the size of the book and the number of subjects dealt with the treatment is necessarily sketchy, but so far as the writer of this notice has observed, it is accurate and may well serve as an introduction to a more serious and detailed study of the lives of these men. Opinions may differ in some cases as to what is the most important work of a great man, and no doubt questions might be raised in regard to the importance attached to some of the pieces of work referred to in the individual articles, but in the main the author seems to have good judgment and a good grasp of the subject. The book can be recommended especially to students who may wish to gain some idea of the general character of the work done by the leading chemists of the world. I. R.

DIE MECHANIK DER WÄRME. Zwei Abhandlungen von ROBERT MAYER. Herausgegeben von A. VON OETTINGEN. (Ostwald's Klassiker der exakten Wissenschaften. Nr. 180.) Leipzig: Verlag von Wilhelm Engelmann. 1911. pp. 90. Price, M. 1.60.

UEBER EINE NEUE CHEMISCHE THEORIE. Von ARCHIBALD SCOTT COUPER. Herausgegeben von RICHARD ANSCHÜTZ. Mit einem Bilde A. S. Couper's. (Ostwald's Klassiker der exakten Wissenschaften. Nr. 183.) Leipzig: Verlag von Wilhelm Engelmann. 1911. pp. 40. Price, M. 1.

The appearance of these little volumes will be welcomed by chemists. To be sure, they are already available in the original journals, but they are not as accessible in that form as in these reprints. All these articles should be studied, not simply read.

Robert Mayer's great articles on the mechanics of heat are edited by A. von Oettingen. There is a picture of the author and the notes are quite full, including a notice of Mayer's life.

Couper's article on a new chemical theory is edited by Richard Anschütz. As is well known to those who are familiar with the history of chemistry, this article is one of only two or three contributions of the author to the science of chemis-

try. The new theory is practically identical with the one proposed by Kekulé. At the same time the two authors wrote quite independently. As is remarked by the editor, "in the history of organic chemistry, Couper is a meteoric phenomenon." His important articles were published within one year, and until quite recently the world knew very little of his origin and of what became of him. Thanks to Alexander Crum Brown, who has looked into Couper's history, light has been thrown upon the subject.

These volumes are highly recommended to students of chemistry.

I. R.

ABHANDLUNGEN ÜBER DIALYSE (KOLLOIDE). Drei Abhandlungen von TH. GRAHAM. Herausgegeben von E. JORDIS. Mit sechs Textabbildungen. (Ostwald's Klassiker der exakten Wissenschaften, No. 179.) Leipzig: Verlag von Wilhelm Engelmann. 1911. pp. 179. Price, M. 3.00.

These important investigations of Graham on diffusion make a valuable addition to the "Ostwald's Klassiker."

H. C. J.

REFRAKTOMETRISCHES HILFSBUCH. Von DR. W. A. ROTH, ausserord. Professor, und DR. F. EISENLOHR, Privatdozent, an der Universität Greifswald. Mit 27 Figuren, 17 Tabellen, sowie Logarithmen. Leipzig: Verlag von Weit und Co. 1911. pp. viii + 146. Price, M. 6.00.

This little book is written primarily to introduce the organic chemist to the methods of refractometric measurement and research.

In twenty-six brief chapters the authors give all the information which one requires for the intelligent and accurate use of any of the well-known types of refractometer. The book opens with a most lucid treatment of the optical principles involved in measurements of refractive power, together with detailed descriptions of the Pulfrich, Heele, Zeiss and Hilger refractometers and various accessories to these instruments. Methods for the determination of specific gravity are treated at some length and very helpful suggestions are made as to the calibration of pycnometers.

About one-fifth of the book is devoted to an excellent outline of the development of our knowledge of molecular refraction and dispersion. The application of atomic refractions to the determination of the constitution of organic compounds is well illustrated and the influence of conjugation in producing optical exaltation is made the subject of several paragraphs. Numerous illustrations are given of the treatment of density and refractive data, so that after reading this book the veriest

tyro might be intrusted with the calculation of the results of laboratory measurements.

The concluding chapter of the book is devoted to the investigation of the refractive power of solutions and solids.

The appendix is of inestimable value to any one who has occasion to make a series of measurements of refractive indices. Here we find tables for the two forms of Pulfrich refractometer giving the refractive index corresponding to every 10 minutes of arc from 0° to 70°, together with temperature corrections for the different prisms. Similar tables are given for the Heele refractometer.

A table of atomic refractions for the D line of sodium and the α, β and γ lines of hydrogen is also given. To any chemist who has had occasion to calculate specific refractions by means of the Lorenz-Lorentz formula, the table giving the logarithms of $\frac{n^2-1}{n^2+2}$ from 1.3000 to 1.7199 will appeal most strongly. In a pocket on the cover of the book is a copy of the five-place logarithmic tables of Küster. It is to be regretted that the authors did not include the table of antilogarithms from the same source but this is a slight omission which can easily be rectified in a future edition.

While intended primarily for the organic chemist, this is a book which should find a place in the library of every chemist who is interested in the application of refractometry to chemical problems. FREDERICK H. GETMAN.

A MICROSCOPICAL EXAMINATION OF FOODS AND DRUGS. A Practical Introduction to the Methods Adopted in the Microscopical Examination of Foods and Drugs, in the Entire, Crushed and Powdered States. By HENRY GEORGE GREENISH, F.I.C., F.L.S., Professor of Pharmaceutics to the Pharmaceutical Society of Great Britain and Director of the Pharmacy Research Laboratory. With 209 Illustrations. Second Edition. Philadelphia: P. Blakiston's Son & Co. 1910. pp. xx + 386. Price, $3.00.

Professor Greenish is well known as an author of several standard books and a number of excellent papers. The present work is a laboratory manual treating of the general technique employed in the microscopical examination of vegetable drugs and food products and contains a fairly large number of typical examples under each of the classes considered. There are some 15 sections, in which are considered: starches, hairs and textile fibers, spores and glands, ergot, woods, stems, leaves, flowers, barks, seeds, fruits, rhizomes, roots, adulterants of powdered foods and drugs and a general scheme for the examination of powders.

Of course, in the use of this book of Greenish, it is understood that one has had a fairly good training in botany, especially that dealing with the anatomy of plants. It is a common mistake of very many analysts to suppose that in the use of the microscope one is dealing with a physical instrument which, like the polariscope or refractometer, gives us on a scale an equivalent reading of percentage strength or impurity. As a matter of fact, the use of the microscope for analytical purposes requires as careful a training in the biological sciences or in optical crystallography as is required by the chemist in mastering the details of analytical technique.

The present work is a very good laboratory treatise and can be recommended to teachers as well as to laboratory workers. The statements are for the most part quite accurate and the directions which are given can be followed with a reasonable assurance that they will yield satisfactory results in practice.

Without in any way disparaging the usefulness of the work, the reviewer may call attention to certain peculiarities that in some cases might be regarded as errors. In the legend under Cardamom, Fig. 135, we read "Cardamom fruit, transverse section of seed." In this we have a transverse section of the seed but none of the other tissues of the fruit are shown. In the discussion of aleurone grains, on page 191, we read that "absolute alcohol dissolves the fixed oil which usually accompanies them in the seeds." As a matter of fact, very few of the fixed oils are dissolved by alcohol, the exception being in the case of castor oil. The method of the study of aleurone grains given by Professor Greenish is not as simple as that proposed by Dr. Arthur Meyer, which should be followed in the study of this class of cell contents, they being among the most important and interesting that the analyst is called upon to examine. In some cases the illustrations are too numerous, as under mustard, on page 196, where we find one of the old-fashioned and inaccurate illustrations of Berg given, although, fortunately, a good modern illustration of the same subject by Tschirch is given on page 206. Again, in the use of reagents, it sounds rather peculiar to have the author say "irrigate with dilute solution of potash." To speak of the use of microchemical reagents as irrigation would be taken humorously by students in this country. In the chapter on adulterants of Food and Drug Powders, the author might well have enlarged upon the subject and referred especially to "wheat middlings," as it occurs far more commonly as an adulterant of foods and drugs than either coniferous or antiospermous woods, which are said to

have been used rather extensively many years ago. These are all, however, rather in the nature of minor criticisms, as the work contains so many useful suggestions that far outweigh any minor defects which readily show themselves to the specialist.

HENRY KRAEMER.

DESCRIPTIVE MINERALOGY, with Especial Reference to the Occurrences and Uses of Minerals. By EDWARD HENRY KRAUS, PH.D., Professor of Mineralogy and Petrography, and Director of the Mineralogical Laboratory in the University of Michigan. Ann Arbor, Mich.: George Wahr. 1911. pp. viii + 334.

This work is manifestly based upon lecture notes of a course in Mineralogy given by the author in the University of Michigan. Alternate leaves are left blank for additional notes by the student.

The classification of the minerals and the crystallographic treatment are based upon the work of Groth. The book presents a summary of the crystallographic features and physical properties of the various minerals and cites the chief localities in which they are found. The genesis of a few of the minerals is considered briefly. An appendix gives a list of the minerals arranged according to the elements contained in them.

The discussion is clear and concise and will be useful to students. A defect of the work, however, is the absence of a summary of the diagnostic physical and chemical properties by which closely related or easily confused minerals are discriminated.

C. K. SWARTZ.

SICHERHEITSEINRICHTUNGEN IN CHEMISCHEN BETRIEBEN. Von DR.-ING. KONRAD HARTMANN, Geheimer Regierungsrat, Senatsvorsitzender im Reichs-Versicherungsamt, Professor an der Techn. Hochschule zu Berlin. Mit 254 Figuren im Text. (Chemische Technologie in Einzeldarstellungen. Herausgegeber, PROF. DR. FERD. FISCHER, Göttingen.) Leipzig: Verlag von Otto Spamer. 1911. S. viii + 312. Preis: geh., M. 15.50; geb., M. 17.00.

The health and life of people employed in chemical manufacturing establishments is mor or less exposed to danger. Measures for minimizing this danger have been taken by the companies, and regulations have been made by the State to protect the employees from harm liable to be done by mechanical and chemical processes. The aim of the book under consideration, treating of safety-measures in chemical manufacturing establishments, is to give an outline of these measures, and to discuss them from a technical as well as from a legal point of view, German law being made the basis.

In Germany, all industrial work is accompanied by govern-

mental inspection and supervision; a record of safety-measures introduced by the engineer and demanded by the German state ought to cover the ground thoroughly, and thus furnish a good basis of work for other countries in which the state laws are less exact and the manufacturer correspondingly less careful.

German statistics show that in chemical manufacture accidents caused by machinery are more numerous than those caused by chemical processes; however, the slow but steady harmful effect upon the health of the workman of poisonous gases and vapors, characteristic for many chemical processes, requires special attention.

The introduction gives a condensed statement of the laws in force in Germany to protect the workmen from harm; it also deals with the necessity of having well-trained foremen for the supervising of the processes and operations, and gives a brief account of the first aid in case of accident. The main part of the volume is of course taken up with the plant and its inner arrangements. Thus, as to plant, there are treated the construction and building materials for various branches of manufactures; the precautions that have to be taken against fire, and the means of extinguishing fires when once started are spoken of; natural and artificial ventilation receive due consideration. The accidents due to machinery, as already stated, are not numerous on account of the intelligence of the machinists and the state regulations which prescribe every possible precaution. In hauling, hoisting and storing of materials accidents are not at all uncommon, hence special regulations exist to reduce their number. The safety-measures with the ordinary lines of machinery, for working iron and wood, with crushing, rolling, mixing, kneading, etc., are taken up in order. The sources of power, steam as well as electric, are considered. After this treatment of apparatus liable to be used in most plants, special branches of manufacture which generate poisonous gases and vapors, or are liable to accidents, such as explosions, are considered in much detail.

Of a book whose general character is encyclopedic, it is possible only to give a cursory review. Few persons will read it through, most manufacturing chemists will be glad to have it for reference, as a perusal of the matter appertaining to the branches in which an individual is engaged will be helpful and thereby useful.

H. O. Hofman.